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OF

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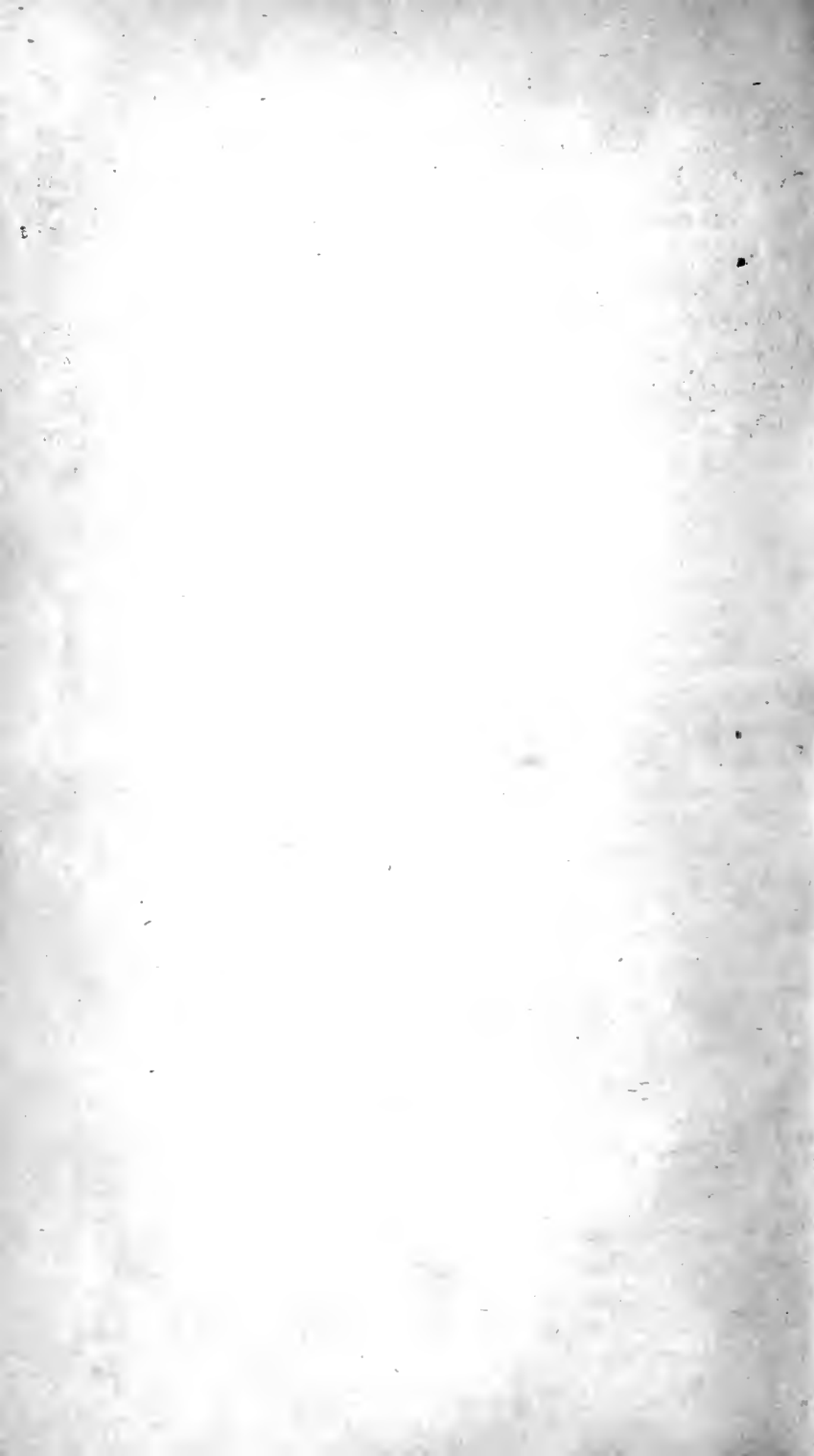
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THE
QUARTERLY JOURNAL
OF
THE CHEMICAL SOCIETY.

I.—*On some new Colouring Matters, Derivatives of Dinitrobenzole, Dinitronaphthaline, &c. &c.*

By ARTHUR H. CHURCH and WILLIAM H. PERKIN.

BY the action of nascent hydrogen upon dinitrobenzole, its homologues and analogues, red or purple colouring matters of great intensity are produced. At present we can give an account of the preparation, composition, and properties of two only of these interesting bodies; but, as we shall show towards the conclusion of this communication, the number of similar bodies producible is very great.

I. *Action of nascent hydrogen on Dinitrobenzole.*—When an alcoholic solution of dinitrobenzole is treated with zinc and hydrochloric acid, the evolution of hydrogen, at first energetic, soon ceases almost entirely, and then the liquid in the immediate neighbourhood of the zinc assumes a rich crimson colour. When the reaction is complete, the liquid must be separated from any excess of zinc, and after complete neutralisation with an alkali, thrown upon a filter and washed with water. The dark-coloured oxide of zinc on the filter must be exhausted repeatedly with strong alcohol. The residue left on evaporation to dryness at 100° C. of this alcoholic solution, may be completely purified by washing with water and exhaustion with absolute alcohol, in which the colouring matter is extremely soluble. This solution evaporated in the water-bath ultimately deposits the whole of the colouring matter in a state of perfect purity. We have examined

the properties of the substance as obtained from its solution in absolute alcohol. For considerations which will shortly be apparent, we have named this substance NITROSOPHENYLINE. Besides the general outlines of the method for the preparation of nitrosophenyline, the following precautions may be noted. If the acid solution of the colouring matter be evaporated to dryness in the presence even of a trace of chloride of zinc, the substance then no longer gives with strong acids the characteristic magnificent crimson tint of nitrosophenyline. Again, the action of the zinc must not be too energetic, nor must the solution get too hot. A saturated cold solution of dinitrobenzole may be taken; the zinc should be perfectly pure, and in the form of a long strip, which, when occasion requires, may be conveniently and rapidly withdrawn. The hydrochloric acid should be strong, and added carefully, drop by drop, until the whole of the dinitrobenzole has been converted: when the reaction is complete, a drop of the coloured solution will not produce any turbidity with water.

Properties of Nitrosophenyline.—As obtained by the evaporation of its alcoholic solution, nitrosophenyline occurs in the form of a black, shining film, brittle, and easily removed from the containing vessel. Although when pure it stands a temperature considerably higher than 100° C. without undergoing any change, yet it is not volatile without decomposition. On the application of heat, it fuses, then evolves a white vapour, leaving a very bulky carbonaceous residue, which may be completely burnt in a stream of oxygen or by prolonged ignition in the air. The new body is almost insoluble in water, but very soluble in acids and in alcohol. To benzole, &c., it imparts scarcely a trace of colour. Heated strongly with soda-lime, all the nitrogen of nitrosophenyline appears in the forms of ammonia and aniline. The formation of aniline was detected by its well-known reaction with hypochlorite of lime. Nitrosophenyline appears to have, if any, a very slight claim to the basic character.

The alcoholic solution of nitrosophenyline exhibits some remarkable optical properties. Perfectly transparent to transmitted light, it presents, when viewed in reflected light, a most extraordinary degree of opacity. A solution of 0.01 of a gramme dissolved in 5 grammes of alcohol, the solution thus containing only 0.2 of a per cent. of nitrosophenyline, exhibits this phenomenon in a very marked manner: a brilliant orange-red light illuminates the surface of the liquid, and descends to a slight depth beneath it; while the liquid itself appears as if finely

powdered vermilion were suspended in it. The flame of alcohol saturated with a baryta-salt is suitable for exhibiting the curious properties of this solution: but they are best seen when examined with the solar spectrum, the *red* ray producing no effect.

The colouring matter is acted upon by acids and by alkalies. The strongest hydrochloric acid and dilute nitric and sulphuric acids dissolve it with a magnificent crimson tint; ebullition with nitric acid produces a yellow colour; and solution in Nordhausen sulphuric acid, an intense brown, which nearly disappears on addition of water. Potash, soda, and ammonia partly precipitate the colouring matter from its acid solutions in brownish-yellow flakes; but if the action of the alkali be not prolonged, the original crimson tint of the solution reappears on the addition of an acid. From a solution of nitrosophenyline in hydrochloric acid, the colouring matter gradually separates as a reddish film, having the brilliant metallic lustre of copper. If nitrosophenyline be dissolved in the strongest hydrochloric acid, and the solution be exposed to the air, a gummy mass is formed after some time, while a portion of the nitrosophenyline separates: the hydrochloric acid in this compound does not exist in any definite proportion.

By the prolonged action of nascent hydrogen, nitrosophenyline loses its colorific properties, possibly passing into a substance containing no oxygen (and possessing the basic character?). The difficulty of preparing pure nitrosophenyline in sufficient quantity has prevented us from inquiring into the exact nature of this new product, but the inquiry would not be without interest. We have not as yet succeeded in regenerating from this colourless compound, by the action of oxidising agents, the original nitrosophenyline. All the analogues of nitrosophenyline which we have obtained suffer further reduction, producing colourless compounds by the prolonged action of hydrogen.

It was not surprising to find that dinitrobenzole is not the only substance of the benzole type from which a colouring matter may be produced in the way described. In the following table is a list of substances, homologous with dinitrobenzole, all of which give similar reactions with nascent hydrogen:—

| | |
|-------------------|-----------------------|
| 1. Dinitrobenzole | $C_{12} H_4 2NO_4$ |
| 2. Dinitrotoluole | $C_{14} H_6 2NO_4$ |
| 3. Dinitroxylene | $C_{16} H_8 2NO_4$ |
| 4. Dinitrocumole | $C_{18} H_{10} 2NO_4$ |
| 5. Dinitrocymole | $C_{20} H_{12} 2NO_4$ |

The hydrocarbons from which the above-mentioned substances were produced had been obtained from very various sources. On account of the sparing solubility of *dinitroxylene*, &c., the compounds corresponding to nitrosophenyline in the higher terms of the series, are produced but sparingly by the method above given.

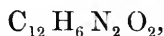
Composition of Nitrosophenyline.—Unlike most colouring matters, nitrosophenyline offers no difficulties in its analysis. In burning it, a stream of oxygen was employed towards the close of the combustion; in this way, the carbonaceous residue which it leaves on ignition was rapidly consumed. The nitrogen was determined by igniting the substance with soda-lime and precipitating the mixed hydrochlorates of aniline and ammonia with bichloride of platinum. As each equivalent of platinum corresponded to 1 eq. of nitrogen, the percentage of this latter element in the original substance was calculated from the amount of metal left on the ignition of the platinum-salts just mentioned. The following are the details of our analyses:—

- I. 0.293 grm. of nitrosophenyline gave
 0.634 „ „ carbonic acid, and
 0.1235 „ „ water.
- II. 0.2825 „ „ nitrosophenyline burnt with soda-lime gave
 0.454 „ „ platinum.

In 100 parts:

| | I. | II. |
|--------------------|-------|-------|
| Carbon | 59.04 | |
| Hydrogen | 4.68 | |
| Nitrogen | | 22.80 |

These percentages lead to the formula



as may be seen in the following table:—

| | | Theory. | Experiment. |
|--------------------------------|-----|---------|-------------|
| 12 equiv. of carbon . . . | 72 | 59.01 | 59.04 |
| 6 „ „ hydrogen . . . | 6 | 4.92 | 4.68 |
| 2 „ „ nitrogen . . . | 28 | 22.95 | 22.80 |
| 2 „ „ oxygen . . . | 16 | 13.12 | — |
| 1 equiv. of nitrosophenyline . | 122 | 100.00 | |

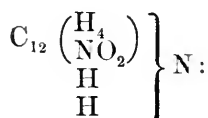
This formula is confirmed by the mode in which nitrosophenyline is formed from dinitrobenzole, $\text{C}_{12}\text{H}_4\text{2NO}_4$, or from nitra-

niline, $C_{12}H_6N_2O_4$, and by the decompositions which it undergoes. As it forms no salts, the formula could not be controlled.

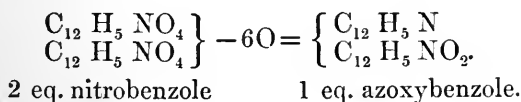
The relations of nitrosophenyline to dinitrobenzole and to nitraniline becomes simple and intelligible if we arrange the crude formula of nitrosophenyline as derived from the foregoing analyses, thus —



or thus —



consequently, it differs from dinitrobenzole by containing 6 equiv. oxygen less, and 2 eq. hydrogen more; and from nitraniline by containing 2 eq. oxygen less. Thus, in the production of nitrosophenyline from dinitrobenzole, 1 eq. of NO_4 is replaced by 1 eq. NH_2 , while the 2nd eq. loses 2 eq. of oxygen; the 1 eq. NO_4 in nitraniline is similarly reduced to NO_2 . Nitrosophenyline may, in fact, be viewed as aniline in which 1 eq. of hydrogen is replaced by 1 eq. of NO_2 ; to such replacements Laurent has applied the terms "*substitutions nitrosées*." From this expression we have constructed the name of the new colouring matter; but as this substance presents but a very equivocal basic character, we have preferred to call it nitrosophenyline rather than nitrosaniline. We are not without an example of a partial reduction of NO_4 , somewhat similar to the present case. For, in the formation of azoxybenzole from nitrobenzole, we may imagine, with Laurent, that the reaction may be described in the following manner:—



The following list presents in a tabular form the derivation of nitrosophenyline, and the composition of those members of the benzole series which are related to it:—

- | | |
|-------------------|---|
| 1. Benzole | $C_{12}H_5, H.$ |
| 2. Nitrobenzole | $C_{12}H_5, NO_4.$ |
| 3. Dinitrobenzole | $C_{12} \begin{matrix} H \\ NO_4 \end{matrix}^4, NO_4 + 8H = C_{12} \begin{matrix} H \\ NO_2 \end{matrix}^4, NH_2 + 6HO.$ |

4. Nitraniline $C_{12}H_4NO_4, NH_2 + 2H = C_{12}H_4NO_2, NH_2 + 2HO$.
5. Nitrosophenyline $C_{12}H_4NO_2, NH_2$.

It is perhaps worthy of remark that nitrosophenyline presents considerable resemblance to the *red indigo* of Berzelius.

II. As we have said before, not only the homologues but the *analogues* of dinitrobenzole produce remarkable colouring matters when acted upon by nascent hydrogen. In order to ascertain the true nature of the new bodies thus produced, we have submitted to a detailed inquiry a beautiful red substance obtained by reducing *dinitro-naphthaline* with hydrogen. But a colouring matter perfectly identical may be procured by acting upon naphthalamine with nitrous acid, or upon the hydrochlorate of naphthalamine with nitrite of potash. By this last method we have obtained it in considerable quantities. This new substance resembles nitrosophenyline in its properties, and is perfectly analogous with it in composition, as we shall shortly show. We have termed it NITROSONAPHTHYLINE.

Properties of Nitrosonaphthyline.—When nitrite of potash is added to hydrochlorate of naphthalamine, nitrosonaphthyline is precipitated, nearly pure. It then merely requires washing with water, drying, and exhaustion with boiling spirits of wine. From this alcoholic solution, by slow evaporation in the water-bath, the colouring matter is gradually precipitated in minute crystals, very dark in colour, and having a green metallic lustre, similar to that of murexide. It imparts to alcohol a rich red tint, which is changed to a magnificent violet by acids, and restored to its original colour by alkalis. Water precipitates it from its alcoholic solution of a scarlet colour. Cotton, linen, paper, &c., may be permanently dyed of an orange tint by immersion in the alcoholic solution of nitrosonaphthyline. Materials so dyed, if plunged in acids, become of an intense purple hue, but in a stream of water the original orange tint speedily returns. Nitrosonaphthyline is insoluble in water. It may be fused without decomposition. Heated strongly, a portion sublimes unchanged; white fumes are afterwards given off, and a residue of carbon remains. Nitrosonaphthyline is not dissolved by dilute acids; strong nitric acid destroys it, but it is soluble in Nordhausen sulphuric acid, with a bluish-purple colour. Alkalis do not change the colour of

nitrosonaphthylene: but by the prolonged action of nascent hydrogen it is destroyed.

Composition of Nitrosonaphthylene.—The determinations of carbon, hydrogen, and nitrogen in this substance were made with the usual precautions, and gave the following numbers:—

- I. 0·301 grm. of substance gave
 0·77 „ „ carbonic acid, and
 0·13 „ „ water.
- II. 0·3205 „ „ substance burnt with soda-lime, gave
 0·37 „ „ platinum.

These numbers correspond in 100 parts to

| | I. | II. |
|----------------|-------|-------|
| Carbon . . . | 69·76 | — |
| Hydrogen . . . | 4·80 | — |
| Nitrogen . . . | — | 16·39 |

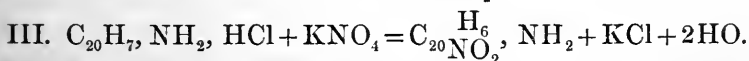
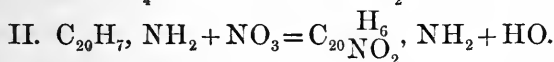
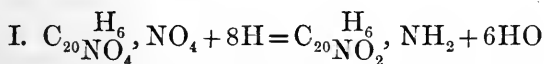
These percentages lead to the formula



as may be seen by the following table:—

| | Theory. | | Experiment. |
|----------------------------|---------|--------|-------------|
| 20 equiv. of carbon . . . | 120 | 69·77 | 69·76 |
| 8 „ „ . . . | 8 | 4·65 | 4·80 |
| 2 „ „ . . . | 28 | 16·28 | 16·39 |
| 2 „ „ . . . | 16 | 9·30 | — |
| 1 „ „ nitrosonaphthylene . | 172 | 100·00 | |

Nitrosonaphthylene is quite analogous to nitrosophenylene: if the former be *aniline* in which 1 equiv. of hydrogen has been replaced by NO_2 , the latter is naphthalamine, in which a similar substitution has taken place. The following equations sufficiently explain the various methods for the formation of nitrosonaphthylene:—



A fourth method, which might be successful, suggests itself,

viz. the action of nascent hydrogen upon nitronaphthalamine. The reaction of aniline and NO_3 produces carbolic acid $\text{C}_{12}\text{H}_6\text{O}_2$, and not *nitrosophenyline*.

Nitrosonaphthyline dissolved in alcohol appears gradually to suffer partial decomposition. In the altered substance thus produced, the carbon amounts to 75 per cent.

The results of the present inquiry indicate the existence of an almost entirely new type of substitution-products,—bodies, too, remarkable alike for their physical properties and their chemical relations.

II. — *Action of Chloride of Cyanogen on Naphthalamine.*

By WILLIAM H. PERKIN.

MM. CAHOIRS and CLOEZ, in their investigations on naphthalamine, observed that it combined with chloride of cyanogen, forming the hydrochlorate of a new base. They, however, did not investigate this subject any further; and as it was interesting to know whether compounds similar to those obtained from melaniline might be produced, I undertook, at the request of Dr. Hofmann, to examine this reaction more minutely.

Preparation of Naphthalamine. — The preparation of naphthalamine is effected by distilling nitronaphthaline with iron and acetic acid, according to the process of Zinin, modified by Béchamp.

This process yields the base in considerable quantity, but in an impure condition. To purify this, it must be dissolved in hydrochloric acid and water, and filtered from all insoluble impurities; the filtrate is then evaporated to dryness, and distilled with lime, when the base comes over nearly pure and perfectly anhydrous.

Preparation of Menaphthalamine. — In subjecting naphthalamine to the action of chloride of cyanogen, I adopted the same arrangement that Dr. Hofmann had used in the preparation of melaniline; namely, a series of tubes filled with the alkaloid through which the chloride of cyanogen was drawn by means of an aspirator. However, in this case it is necessary to support the action from the commencement by the application of heat, naphthalamine being a solid substance.

When the gas is passed into the fused anhydrous naphthalamine, chemical action is at once rendered perceptible by a rapid eleva-

tion of the temperature, and the gradual thickening of the liquid, which prevents the gas from passing freely. To complete the reaction, heat must be carefully applied sufficient to keep the compound in a state of fusion.

On cooling, the naphthalamine is found converted into a black resinous mass, which consists principally of the hydrochlorate of a base, which I propose to call menaphthalamine.

On boiling this mass in a large quantity of water, it almost entirely dissolves. On adding potassa or ammonia to the filtered liquid, a white precipitate is produced, which is freed from chloride of potassium, or ammonium, by washing with water, and recrystallised once or twice from alcohol, from which it is deposited in small white needles.

This base, when dried at 100° C. and burnt with protoxide of copper, gave the following numbers:—

| | | |
|-----|--------|------------------------------|
| I. | 0.249 | grm. of menaphthalamine gave |
| | 0.7385 | „ carbonic acid, |
| | 0.1275 | „ water. |
| II. | 0.2840 | „ menaphthalamine gave |
| | 0.8425 | „ carbonic acid, |
| | 0.1410 | „ water. |

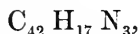
These numbers lead to the following percentage composition:—

| | I. | II. |
|----------------|-------|-------|
| Carbon . . . | 80.88 | 80.90 |
| Hydrogen . . . | 5.40 | 5.50 |

Two analyses of the platinum-salt gave a mean of 19.065 per cent. of platinum.

| | |
|---|----------|
| Equivalent deduced from the platinum-salt | = 311.24 |
| Theoretical equivalent | = 311.00 |

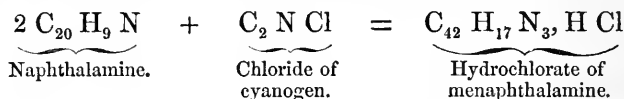
These results lead to the formula



which require the following values:—

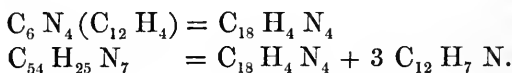
| | Theory. | | Mean of experiments. |
|---------------------------|-------------|-------------|----------------------|
| 42 equiv. of carbon. . . | 252.0 | 81.0 | 80.89 |
| 17 equiv. of hydrogen . . | 17.0 | 5.4 | 5.45 |
| 3 equiv. of nitrogen . . | 42.0 | 13.6 | |
| | <hr/> 311.0 | <hr/> 100.0 | |

This shows that the formation of menaphthalamine is perfectly analogous to that of melaniline and metoluidine, 2 equiv. of naphthalamine and 1 equiv. of chloride of cyanogen yielding 1 equiv. of the hydrochlorate of menaphthalamine.



Properties of Menaphthalamine. — This base, when pure, crystallises in small white needles, which are not coloured by exposure to the atmosphere.

Menaphthalamine is odourless; it has a bitter taste; fuses at about 200° C. into a transparent slightly yellowish oil. If the temperature be raised above 260° C., decomposition ensues, pure naphthalamine distils over, and a brown mass remains in the retort. In the case of melaniline, the residue had the formula $\text{C}_{54} \text{ H}_{25} \text{ N}_7$, which may be regarded as a compound of aniline-mellone with 3 equiv. of aniline.



It is probable that the menaphthalamine residue has an analogous composition.

Menaphthalamine is almost insoluble in water, and only moderately soluble in alcohol and ether. It changes the colour of red litmus-paper. Chromic acid acts but slowly upon it.

COMBINATIONS OF MENAPHTHALAMINE.

This base forms salts with all acids, many of which are amorphous or very slightly crystalline. They are all sparingly soluble in water.

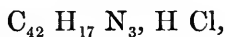
The salts have no action on litmus-paper. They are precipitated by acids and saline solutions; potassa and ammonia decompose them, the base being separated in the form of a pure white powder.

Hydrochlorate of Menaphthalamine. — This salt is a white amorphous compound, which becomes slightly red when exposed to air and moisture. It is moderately soluble in water, and very soluble in alcohol and ether: when heated, it is decomposed, hydrochlorate of naphthalamine subliming, and leaving a black residue in the retort.

A determination of hydrochloric acid gave the following result:—

0·4422 grm. of hydrochlorate gave
 0·682 ,, chloride of silver, corresponding to
 10·44 per cent. of hydrochloric acid.

This number leads to the formula



which requires the following values:—

| | Theory. | | Experiment. |
|-------------------------------------|---------|-------|-------------|
| 1 equivalent of menaphthalamine = | 311·0 | 89·6 | — |
| 1 equivalent of hydrochloric acid = | 36·5 | 10·4 | 10·44 |
| | <hr/> | <hr/> | |
| | 347·5 | 100·0 | |

Sulphate.—This salt is best obtained by neutralising sulphuric acid with menaphthalamine. It is a white, perfectly amorphous salt, moderately soluble in alcohol and ether, which on evaporation deposit it in the form of a white powder.

Nitrate.—This salt, which is the finest of all the menaphthalamine salts, may be prepared by adding menaphthalamine to very dilute boiling nitric acid. This solution, on standing, deposits the nitrate in small white prisms, nearly insoluble in cold water, but very soluble in alcohol and ether.

Phosphate.—It is a white crystalline salt, very soluble in alcohol and ether.

Binoxalate.—This salt is best obtained by boiling menaphthalamine with an excess of oxalic acid. From this solution the salt crystallises in small tufts of white needles, which are not easily soluble in water, but moderately soluble in alcohol and ether.

Hydrobromate and Hydriodate.—These salts are crystalline, and very soluble in alcohol.

Hydrochloroplatinate.—This compound is best prepared by adding an alcoholic solution of bichloride of platinum to a warm alcoholic solution of the hydrochlorate of menaphthalamine; from this solution, small yellow crystalline scales are deposited. If, however, the aqueous solutions are employed, it is immediately precipitated as an amorphous powder, which is almost white, but soon becomes slightly green.

Two determinations of the platinum gave the following numbers:—

| | | | | |
|-------------------------------|---------|-----------------------|---|-------|
| I. | 0.229 | grm. of the salt gave | | |
| | 0.0435 | „ „ | platinum. | |
| II. | 0.19975 | „ „ | salt gave | |
| | 0.03775 | „ „ | platinum. | |
| | | Theory. | Experiment. | |
| | | | <div style="text-align: center;"> I. II. </div> | |
| Percentage of platinum in the | | } 19 08 | 19.04 | 19.09 |
| platinum-salt . . . } | | | | |

Terchloride of gold gives with menaphthalamine-salts a blue precipitate.

METAMORPHOSES OF MENAPHTHALAMINE.

Menaphthalamine, when exposed to the action of various agents, undergoes a variety of transformations, many of which I have not been able to study.

Action of Sulphuric Acid.—When Nordhausen sulphuric acid is brought in contact with menaphthalamine, it becomes pasty, owing to the formation of the sulphate; but if a gentle heat be applied it becomes perfectly liquid. This liquid, on being diluted with water and treated with carbonate of lead, produces a soluble lead-salt, of a new acid, which decomposes partially every time it is evaporated.

On passing sulphuretted hydrogen through a solution of the lead-salt, a colourless solution is obtained (with precipitation of the lead as sulphide). When this liquid is evaporated, the new acid is decomposed into a soluble alkaline body, and an insoluble neutral one.

Action of Fuming Nitric Acid.—This acid acts violently on menaphthalamine, producing a variety of substitution-products.

Chlorine, bromine, and iodine seem to produce neutral compounds.

Action of Cyanogen.—If cyanogen is passed through an alcoholic or ethereal solution of menaphthalamine, it becomes first yellow, and then red, nothing being deposited on standing; but if the base is made into a thin paste with ether, and cyanogen passed through it, it all dissolves; and, on standing, the solution deposits a slightly crystalline body of a light buff colour, which may be purified by washing with ether.

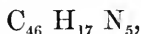
A combustion of a specimen dried at 100° C. gave the following results:—

| | |
|--------|-----------------------------|
| 0.274 | gram. of the substance gave |
| 0.764 | „ carbonic acid, and |
| 0.1292 | „ water, |

which gives the following percentage composition:—

| | | | | | |
|----------|---|---|---|---|-------|
| Carbon | . | . | . | . | 76.00 |
| Hydrogen | . | . | . | . | 4.71 |

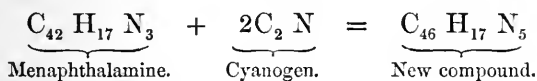
This may be translated into the formula



as may be seen by the following table:—

| | | Theory. | Experiment. |
|---------------------|---|-----------|--------------|
| 46 equiv. of carbon | . | 276 | 76.00 |
| 17 „ hydrogen | . | 17 | 4.69 |
| 5 „ nitrogen | . | 70 | 19.31 |
| | | <hr/> 363 | <hr/> 100.00 |

This compound, therefore, like dicyanomelaniline, is formed by the combination of two equivalents of cyanogen with one of menaphthalamine.



DICYMENAPHTHALAMINE (which name I propose for this compound) is a slightly buff-coloured body, which crystallises with difficulty; it is moderately soluble in alcohol and ether, but insoluble in water.

It is a base, though a very unstable one; it dissolves readily in dilute acids, and may be reprecipitated by ammonia if added directly after solution; but, like cyaniline and dicyanomelaniline, this base cannot remain in acid solutions without undergoing complete decomposition. If this base be dissolved in hydrochloric acid, and the solution allowed to stand for a few moments, it becomes cloudy, and a yellow substance begins to appear, which is not the hydrochlorate of dicymenaphthalamine.

The best process for the preparation of this new compound consists in adding dilute hydrochloric acid to a warm alcoholic solution of dicymenaphthalamine. On standing, it is deposited in

small scales of a yellow colour. The mother-liquors from the preparation of this compound always contained ammonia.

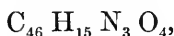
The analysis of this compound dried at 100° C. gave the following results :—

| | |
|-------|-------------------------|
| 0·212 | gram. of substance gave |
| 0·590 | „ carbonic acid, and |
| 0·080 | „ water. |

These numbers lead to the following percentage composition :—

| | | |
|------------------|---|------|
| Carbon | = | 75·6 |
| Hydrogen | = | 4·2 |

which may be translated into the formula

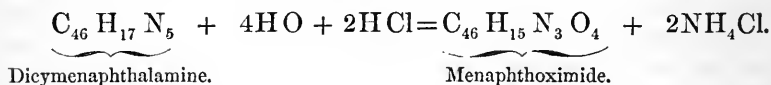


as is evident from the following comparison of the theoretical with the experimental values :—

| | | Theory. | Experiment. |
|-------------------------|-------------|--------------|-------------|
| 46 equiv. of carbon . . | 276·0 | 75·66 | 75·6 |
| 15 „ hydrogen . . | 15·0 | 4·10 | 4·2 |
| 3 „ nitrogen . . | 42·0 | 11·50 | — |
| 4 „ oxygen . . | 32·0 | 8·74 | — |
| | <hr/> 365·0 | <hr/> 100·00 | |

This substance, which I propose to call MENAPHTHOXIMIDE, is perfectly analogous in its properties to melanoximide.

Its formation is, as illustrated by the following equation,—



This substance is insoluble in water, and very slightly in alcohol and ether, from which it may be crystallised, but with difficulty.

Menaphthoximide may be regarded as binoxalate of menaphthalamine minus 4 equivalents of water,—a view which is supported by experiment. On addition of potassa to this compound, menaphthalamine is reproduced, and the mother-liquor is found to contain oxalic acid.

The action of acids upon menaphthoximide is precisely the same as in the case of melanoximide; namely, it is converted into oxalic

acid, menaphthalamine, and a white neutral body, to which I intend to return at some future period.

Action of Heat on Menaphthoximide.—When menaphthoximide is heated to 245°C ., it fuses; if the temperature be raised to 260°C ., it decomposes, with evolution of a white vapour, having a most peculiar and powerful odour. I believe that this reaction is analogous to that which melanoximide undergoes when submitted to the influence of heat, and that the substance produced corresponds to Dr. Hofmann's anilocyanic acid,—in fact, that it is the naphthalamine term corresponding to cyanic acid, or naphthalocyanic acid; but I have not been able to obtain this compound in sufficient quantity to establish this supposition by experiment. I hope, however, to return to the examination of this most interesting subject as soon as possible.

In conclusion, I have to thank Dr. Hofmann for the advice and assistance he has afforded me during the prosecution of this investigation.

III.—*Note on the Solubility of Sulphate of Baryta in Hydrochloric Acid.*

By HENRY M. NOAD, Ph.D.

LECTURER ON CHEMISTRY AT ST. GEORGE'S HOSPITAL.

IN the Proceedings of the Royal Society, vol. viii. p. 532, there is an abstract of a paper "On Chemical Affinity, and the Solubility of Sulphate of Baryta in Acid Liquors," by Mr. F. Crace Calvert. The author says that "the insolubility of this salt is affected even by the weakest nitric or hydrochloric acids," and that "in future the practice of rendering liquors acid with either of these acids must be discontinued when sulphates are to be determined." In the abstract of Mr. Calvert's memoir, as it appears in the "Proceedings," the only experiments quoted relate to the solubility of sulphate of baryta in *nitric* acid; whether he extended his researches to hydrochloric acid, it is not stated; it is to be concluded that he did so, since, in a practical point of view, it is of far greater consequence to establish the fact, and the degree of the solubility of this sulphate in the latter acid than in

the former, the great majority of sulphur and of sulphuric acid determinations in mineral analyses being made in liquids containing excess of hydrochloric acid.

That sulphate of baryta is soluble to some extent in nitric acid, or at any rate that sulphuric acid may exist in nitric acid, both strong and dilute, and still no precipitate or even cloudiness be produced by the addition of a barytic salt, has, I believe, been known for some time to many chemists. Speaking for myself, I have certainly been aware of the fact for upwards of two years. I do not claim it as a discovery of my own, though I am quite unable to say from whom I derived my information. I have reason to believe, however, that the discovery originated with Mr. Nicholson, though the first public announcement of it is probably in Mr. Calvert's paper.

It is easy to prove that almost all the fuming nitric acid of commerce contains sulphuric acid, though it may retain a perfect transparency, when largely diluted with water, and treated with a barytic salt. All that is necessary is to evaporate an ounce or so of the acid, in a platinum capsule, down to about a drachm, then add water and nitrate or chloride of barium, upon which a greater or less turbidity will ensue. That very grave errors have been committed in sulphur determinations in organic compounds, in consequence of a want of the knowledge of this important fact, cannot be doubted, fuming nitric acid having been very generally employed as the oxidising agent to convert the sulphur into sulphuric acid: thousands of mineral analyses must, for the same reason, be considered erroneous as regards the determination of this particular element; and I consider myself fortunate that I was made aware of the almost invariable impurity of nitric acid, previous to the commencement of my own iron and cinder analyses, and thus have been enabled to guard against it. It is quite otherwise, however, as regards hydrochloric acid; and I must certainly confess that I read the abstract of Mr. Calvert's paper with considerable discomfort; for if his statement be true, then my own, and many thousand other sulphur determinations, have been made in vain, since in separating sulphur from phosphorus in crude iron and forge cinders I have almost invariably done so in an acid solution, and that acid has been *hydrochloric*. Being thus so immediately interested, and in the absence of all experimental evidence in the abstract of Mr. Calvert's paper, it was natural that I should forthwith commence a series of experiments to satisfy myself as to the justice or injustice of Mr. Calvert's con-

clusions; it being sufficiently evident that if the insolubility of sulphate of baryta is affected by the weakest hydrochloric acid, the usual course of mineral analyses must be somewhat modified. The results of my experiments I beg briefly to lay before the Society; they have proved the groundlessness of my fears, and may have the effect of relieving the minds of some other practical chemists as they have relieved mine. They show that though, under certain circumstances, the insolubility of sulphate of baryta is affected by weak hydrochloric acid, yet that the error likely to be thereby introduced into analysis is either altogether *nil*, or so exceedingly small as to be in most cases unworthy of consideration.

FIRST SERIES OF EXPERIMENTS.

Twelve liquors were prepared of uniform bulk,—the first consisted of 1000 grain measures of distilled water; the second of 900 grains of water + 100 grain measures of hydrochloric acid, sp. gr. 1.153; the third of 800 grains of water + 200 grain measures of the same acid; the fourth of 700 grains water + 300 grain measures of acid; the fifth of 600 grains water + 400 grain measures of acid; the sixth of 500 grains water + 500 grain measures of acid; the seventh of 400 water + 600 acid; the eighth of 300 water + 700 acid; the ninth of 200 water + 800 acid; the tenth of 100 water + 900 acid; the eleventh of 1000 grain-measures of the acid without any water: 5 grains of neutral and thoroughly dried sulphate of potash were dissolved in each of these liquors; and, while boiling, solutions of 10 grains of nitrate of baryta in 300 grains of water were poured into each; they were allowed to remain at rest for twenty-four hours, then filtered, and the sulphate of baryta washed, dried, ignited, and weighed. In the twelfth experiment, the 5 grains of sulphate of potash were dissolved in 500 grain measures of hydrochloric acid, and the 10 grains of nitrate of baryta were boiled for some time with another 500 grain measures of the acid; little, if any, of the salt was dissolved, but abundance of chlorine was disengaged, and the liquor became dark yellow from the absorption of nitrous vapour. The acid liquor was decanted and added to the acid solution of the potash salt, sufficient boiling water was then added to dissolve the baryta-salt, and the liquors were then mixed, boiled, and the sulphate of baryta allowed to subside. The quantities of barytic sulphate obtained in the twelve experiments are given in the following table. The quantity of nitrate of baryta required theo-

retically to precipitate 5 grains of sulphate of potash is 7.5 grains, and the quantity of sulphate of baryta produced should be 6.70 grains.

| Number of experiment. | Number of grain measures of water. | Number of grain measures of hydrochloric acid. Sp. gr. 1.153. | Quantity of sulphate of potash used. | Quantity of nitrate of baryta used. | Quantity of sulphate of baryta produced. |
|-----------------------|------------------------------------|---|--------------------------------------|-------------------------------------|--|
| 1. | 1000 | 0 | 5 grs. | 10 grs. | 6.74 |
| 2. | 900 | 100 | do. | do. | 6.70 |
| 3. | 800 | 200 | do. | do. | 6.71 |
| 4. | 700 | 300 | do. | do. | 6.72 |
| 5. | 600 | 400 | do. | do. | 6.69 |
| 6. | 500 | 500 | do. | do. | 6.71 |
| 7. | 400 | 600 | do. | do. | 6.78 |
| 8. | 300 | 700 | do. | do. | 6.77 |
| 9. | 200 | 800 | do. | do. | 6.76 |
| 10. | 100 | 900 | do. | do. | 6.78 |
| 11. | 0 | 1000 | do. | do. | 6.78 |
| 12. | | 500 | do. | do. | 6.78 |

It is seen that so far from there being a loss of sulphate of baryta, there is in the last six experiments a small apparent excess; this doubtless arose from a small portion of undecomposed nitrate having been carried down mechanically in the strongly acid liquor with the sulphate, from which it was not subsequently thoroughly removed by washing. It is well known that nitrate of baryta does adhere most pertinaciously to the sulphate when thus carried down, and requires long-continued washing to detach it; it is also well known that nitrate of baryta is very sparingly soluble in highly acid liquids. The precipitates were in all cases washed with the same quantity of boiling water, and the experiments show clearly, I think, that in this particular bulk of liquid, — viz. about 1000 grains measure, — the precipitation of sulphuric acid is complete in whatever proportion hydrochloric acid exists, — whether it forms the entire volume of the liquid, or whether it is absent altogether.

But Mr. Calvert says, "The solubility of sulphate of baryta is affected in a higher degree by the *bulk* of the acid than by its strength," and the table that he gives for nitric acid fully proves this to be the case. It became necessary to examine this position in relation to hydrochloric acid.

SECOND SERIES OF EXPERIMENTS.

5 grains of sulphate of potash were dissolved in 9000 grains of distilled water + 1000 grains of hydrochloric acid, sp. gr. 1.153, and precipitated as before, while boiling, with a solution of 10 grains of nitrate of baryta. Three precisely similar experiments were made, and the following quantities of sulphate of baryta were obtained:—

| I. | II. | III. |
|------------|------------|------|
| 5.81 . . . | 5.72 . . . | 5.90 |
| Mean . . . | 5.81 grs. | |

Here, then, there is a distinct loss of .89 gr. of sulphate of baryta, but does this arise from a solution of the salt in the acid liquor, or is it the result of dilution? To determine this point, the same quantities of sulphate of potash were dissolved in the same bulks of acid and water, but double the quantity, viz. 20 grains of the precipitant, were employed: the proportions of sulphate of baryta now obtained in three experiments were—

| I. | II. | III. |
|------------|------------|--------------------|
| 6.52 . . . | 6.51 . . . | 6.50 |
| Mean . . . | 6.51 grs. | Loss19 gr. |

Three other solutions were then made and precipitated by 30 grs. of nitrate of baryta. The quantities of sulphate of baryta obtained were—

| I. | II. | III. |
|------------|------------|------|
| 6.71 . . . | 6.69 . . . | 6.71 |

the exact theoretical quantity. I must observe, that in these last six experiments the washings were continued for some hours, in order to avoid any possible error arising from the adhering of a portion of the precipitant to the precipitated salt.

By the side of these last experiments I placed two others, in one of which the 5 grains of sulphate of potash were dissolved in 10,000 grains of boiling distilled water, and in the other in

20,000 grains, no acid being added in either case: the quantities of sulphate of baryta obtained were —

| I. | II. |
|-----------|-----------|
| 6·73 grs. | 6·72 grs. |

Lastly, the following experiment was made:—

5 grains of sulphate of potash were dissolved in a small quantity of water, and precipitated by 10 grains of nitrate of baryta; 10,000 grain measures of a mixture of 9 parts water and 1 part hydrochloric acid were then added, and the whole was boiled for 20 minutes; after 24 hours the resulting sulphate of baryta was weighed. Two precisely similar experiments were made, with the following results:—

| I. | II. |
|----------|----------|
| 4·4 grs. | 4·5 grs. |

Here, then, was a loss of 2·3 grains of sulphate of baryta, one-third of the entire quantity that should have been obtained. The solubility of sulphate of baryta in a large bulk of dilute hydrochloric acid is proved conclusively by this experiment, but in a practical point of view it is not a matter of any importance; since, in the first place, it is not usual to attempt precipitations in such bulky liquids, but always to concentrate as far as possible; and, in the second place, it is always the practice to add considerable excess of the precipitant, which, as has been shown above, counteracts the tendency of the barytic sulphate to dissolve in the acid liquor. On the whole, then, I think that we may, without fear, continue to make our sulphur determinations in strong hydrochloric acid liquors, and that the only thing that the analyst has to guard against is the possible existence of sulphuric acid in the nitric acid he may employ as his oxidising agent.

While on the subject of sulphur determinations, I may allude to a method I have lately adopted for estimating the amount of this element in crude iron, which, with certain precautions, gives very accurate results, and which possesses the great advantage of enabling the operator to work upon much larger quantities of material than in any of the usual methods. The pounded iron is digested in a flask with dilute hydrochloric acid, and the gases evolved passed through three Wolfe's bottles, each containing a solution of arsenious acid; the whole of the sulphur of the metal passes over as sulphuretted hydrogen, and is estimated as As S_3 . I have convinced myself, by repeated experiments, that the *whole* of

the sulphur is thus obtained in combination with the arsenic, and that the phosphorus which the crude iron invariably contains, though it is partly liberated, at the same time, in the form of phosphuretted hydrogen, does not interfere with the accuracy of the result. In what form the phosphorus combines with the arsenious acid, or whether it combines with it at all, I intend to make the subject of a special investigation; at present but little is known of the compounds of phosphorus with arsenic. I have, however, satisfied myself that no insoluble compound is formed under the circumstances of the above experiment. The only precautions to be observed are—1st, not to add too much hydrochloric acid to the water in which the arsenious acid is dissolved, the tersulphide not being so insoluble in hydrochloric acid as is generally supposed; nevertheless the solubility of arsenious acid in water is so greatly increased by the addition of a little hydrochloric acid, that a small quantity may be added with advantage; 2nd. the evolved gases must pass through at least three Wolfe's bottles, and it may occasionally be advisable to add a fourth; and, 3rdly, the connections between the bottles must be of *sheet* and not of *vulcanised* India rubber, it being almost impossible to keep the latter perfectly tight under the pressure to which they are subjected. I have occasionally employed solutions of nitrate and acetate of lead in the place of arsenious acid, but the objection to these salts is the great difficulty of washing thoroughly the bulky sulphide of lead: the results are, however, when carefully obtained, quite trustworthy.

IV.—*On the Source of the Water of the deep Wells in the Chalk under London.*

By DUGALD CAMPBELL.

THE source of the supply of water to the deep wells in the chalk below London, is a subject which has occupied the attention of many persons, and has been discussed in several Societies on more than one occasion; but although this Society has recorded in its Journal the analysis of the water of several of the deep wells, still the origin of the source of their supply has not been considered much by the Society.

On this occasion I purpose to give, in as short a manner as I can, some of the views which have hitherto been maintained as to the origin or source of the water; and I shall endeavour to point out, from the results of my experiments upon the water, that its true source has not yet been suggested.

One of the theories most strenuously maintained, and apparently the most popular, is that the wells under London are partly supplied from the infiltration of sea-water, and partly from the infiltration of water from the chalk in the upper strata; and this view is supposed to be substantiated in a great measure by the chemical character of the water.

The advocates of this theory say that in the water of all the chalk-wells in or around London, which are below Trinity high water mark, the quantity of solid saline matter is very large, whereas, in the water of those wells which are above Trinity high water mark, there is comparatively a small quantity of solid saline matter. What they mean by solid saline matter are salts of potash and soda.

They take the water of the Trafalgar-square wells,—which, as far as my experience goes, contains the largest amount of solid saline matter of any water of the deep wells,—as a type of the water from below Trinity high water mark, and the water from wells at Watford in the upper chalk as a type of the water above Trinity high water mark.

They also say that the large amount of saline matter, together with the small amount of carbonate of lime or chalk, in the deep well-water,—just the opposite of what is found in the shallow chalk well-waters,—is another proof of the strong impregnation of the chalk-water with sea-water.

They likewise insist, that this view is considerably strengthened by the fact, that there is a gradual increase of the solid saline matter in the water of the London deep wells, which would not be the case were the water derived entirely from the upper strata, and had no supply whatever from the sea.

In order to show that the saline matter in the deep well-water is on the increase, Professor Brande's analysis of the Trafalgar-square water is quoted in comparison with Messrs. Abel and Rowney's analysis. According to Mr. Brande, in 1846 the solid contents per gallon were 66·1 grains, consisting of 59·9 grains of soda salts and 3·1 grains of carbonate of lime, with 2·4 grains of carbonate of magnesia; by Messrs. Abel and Rowney's analysis, in 1849 the solid contents per gallon were 68·24 grains,—showing an increase on the whole of 2·14 grains of solid matter per gallon;

and "this increase was principally due to salts derivable from sea-water, there being only 0.17 grain increase in the carbonate of lime."

I may just mention, that in Mr. Brande's analysis no volatilised or organic matter is given; and were this supplied, I believe there would be little difference in the amounts of solid contents in the two analyses; indeed, were the organic matter estimated by the method generally employed at that time, and still I believe retained by many analysts, it would amount to more than 2.14 grs.,—the excess of solid contents found by Messrs. Abel and Rowney over that found by Mr. Brande. This method of estimating the organic matter in water, to which I have alluded, was to evaporate a portion to dryness, weigh the residue, and afterwards heat it to low redness till it ceased to lose weight, when the difference from its former weight would be considered the organic matter.

In 1850, my attention was directed to the Trafalgar-square water, and I then found that the solid contents, including organic matter, were per gallon 61.60 grains, or 6.64 grains per gallon less than when it was examined by Messrs. Abel and Rowney in 1849.

In the Society of Civil Engineers, last July, it was again stated that the salts were increasing in the water of the Trafalgar-square deep wells, and I then directed my attention to the subject, procured specimens of the water, and made an analysis of it, when I found that what had been stated was not the case, and the saline contents were less than when I examined it in 1850.

Perhaps I may be allowed a digression here to state that, before this, I had analysed the water from many of the deep wells in different parts of London, and in all I had found a large amount of soda-salts, and a small though weighable quantity of potash-salts, varying in potash from 0.327 grain in a gallon to as much as 1.33 grain; but I was scarcely prepared to find the Trafalgar-square water to have the same character, Messrs. Abel and Rowney having found 13.67 grains of sulphate of potash in a gallon;* however, on procuring a copy of the minutes of the Proceedings of the Civil Engineers, vol. ix., I for the first time saw Mr. Brande's analysis, and either he had not detected any potash-salts in the water, or they were in such small quantities as not to be considered by him worth noticing, for they are not given in the analysis.

* Chem. Soc. Qu. J. i. 97, *et seq.*

I have placed in a table my analysis of the Trafalgar-square well-water, together with an analysis of the Watford chalk-water, and also an analysis by Dr. Schweitzer of the water of the English Channel; so that at one glance a comparison of their composition may readily be made, in order the better to test the different views which have been set forth as to the source of the supply of the deep well-water in the chalk under London.

TABLE OF ANALYSES.

| Substances found. | Trafalgar-sq. water, grs. in a gallon at 60° Fah. | Watford water, grs. in a gallon at 60° Fah. | Eng. Channel sea-water, grains in a gallon. |
|-------------------------------------|--|--|--|
| Carbonate of soda - | 10.58 | | |
| Sulphate of soda - | 21.34 | 0.70 | |
| Chloride of sodium - | 19.04 | 1.39 | 1894.13 |
| Carbonate of potash - | 1.05 | | |
| Chloride of potassium - | | | 53.55 |
| Carbonate of magnesia | 2.07 | | |
| Sulphate of magnesia - | | | 160.65 |
| Chloride of magnesium | | | 256.62 |
| Bromide of magnesium | | | 2.03 |
| Carbonate of lime - | 2.74 | 18.20 | 2.31 |
| Sulphate of lime - | | | 98.42 |
| Nitrate of lime - - | | 1.76 | |
| Phosphate of iron and lime - - - | 0.97 | | |
| Silica - - - | 0.40 | 0.81 | |
| Volatilised matter - | 0.66 | 0.81 | |
| Total - - | 58.85 | 23.67 | 2467.71 |

In the analysis, I have combined the acids with the bases, but not before getting as good an insight into the constitution of the water as can be obtained, by taking its degree of hardness and alkalinity before, and likewise after submitting it to the softening process of Dr. Clark.

I may observe, that the volatile or organic matter is obtained as follows: -- The water is evaporated to dryness in a platinum

capsule, and the solid contents dried until they cease to lose weight at the temperature of 260° Fah.; the weight is then noted, and the capsule heated to low redness until no more loss of weight takes place; the contents are then saturated with fresh carbonic acid water, and dried at 260° ; and this operation of saturating with carbonic acid water and drying is repeated until an uniform weight is obtained: the difference between this and the first weight before heating to low redness, is volatilised or organic matter. This is not an exact method of estimating volatile or organic matter, there being none; still I think it is the most correct known; for if the residues, after evaporating the water, are simply heated to redness and weighed, no two results are obtained alike from the same water. The process given is better in this respect: besides, the water originally is not caustic, whilst a solution of the residue in water which has been heated to redness generally is, — indicating that it has been deprived of acid. In the residues from water, I find carbonic, nitric, and even sulphuric acid, affected by the heating to redness. Restoring the carbonate as described was suggested by Dr. Clark.

The results which I obtained, as I stated before, show that the salts in the water have decreased, since 1850, 2.75 grs. per gallon, and since 1846 altogether 9.39 grs. per gallon, — a result rather fatal to the statement that the salts are increasing in the water, and also to the idea of a percolation of sea-water into the wells.

But I think it is only necessary to compare an analysis of the deep well-water with that of a proper chalk-water, together with an analysis of sea-water, as in the table I have given, to be convinced that the deep well-water is no mixture of chalk and sea-water; and it is quite clear, without making an experiment, that under no circumstances could a mixture of sea-water with chalk-water in any proportion produce the deep well-water. To account for the presence of carbonate and sulphate of soda alone in the deep well-water, without going further into the matter, is impossible.

As a modification of the first view given, it has been suggested that the water may still be a mixture of chalk-water and sea-water, only the sea-water has undergone a change by percolating through the chalk strata before reaching the wells. There can be no doubt that the first portions of sea-water passing through chalk would be deprived of their salt to a great extent, if not entirely; but as the chalk became saturated with sea-water, the water would, in passing through, increase in its saline properties, and in time

would become sea-water. But this, I have shown, is not the case: besides, the analysis of the three waters will not admit of this view; for common salt is not decomposed in an ordinary way by carbonate of lime or sulphate of lime. But granting for a moment, for the sake of argument, that, by some means which we know not of, it underwent decomposition, still the chlorine which was originally combined with the decomposed chloride of sodium—and it is not a small quantity—is not to be traced in the analysis of the deep well-water, but has entirely disappeared out of it,—a thing I would consider chemically impossible.

An observation I have made, and which I do not think has been noticed before by anyone writing upon the subject, is, that the deeper wells in the chalk contain more saline matter in a gallon than the shallow ones,—rather a strong fact, I consider, against the view of the infiltration of sea-water into the wells, for sea-water should become less saline in proportion to the thickness of chalk it has to percolate through, and not more saline.

Another view of the source of the deep well-water, which has been supported by no mean chemical authority, is, that it is ordinary chalk-water which has been decomposed by percolating through the chalk strata, and has no sea-water in its composition.

The explanation given of how it is changed is as follows:—Silicate of soda is found in the chalk through which the water percolates; this silicate is decomposed by the carbonate of lime in the water, insoluble silicate of lime deposits, and the carbonate of soda gets into solution in its place.

This may be very well to account for the increase of the carbonate of soda, and decrease of carbonate of lime in the deep well-water, but it does not in any way afford a solution for the presence of chloride of sodium and sulphate of soda in such large quantities as these salts are found in the deep well-water.

My own conviction is, that the water does not originally come from an ordinary chalk stratum; indeed, I believe that the deep wells have a separate and independent source, and are not supplied from the upper chalk-water at all. This view has been strengthened by my having observed a peculiarity in the water of the deep wells not hitherto, I think, noticed,—namely, that there is scarcely the slightest, if any, indication of nitrates in the proper deep well-water; whereas all waters from the upper chalk which I have examined, and these are not a few, contain a notable quantity of nitrates,—indeed, it is a characteristic of a proper chalk-water to do so. The Watford water, one of the purest chalk-waters to be

met with, gave on an average of several examinations 1.76 grain of nitrates per gallon, as noted in the table.

As the deep well-water contains phosphates (an observation which was made by Mr. Graham*), and as phosphates are generally associated with animal or vegetable substances, I should have expected an increase of nitrates in this water over the ordinary chalk-water, from the oxidation of nitrogenous matter accompanying the phosphates; but the freedom from nitrates, especially under the circumstances, is certainly very peculiar, and the inferences to be drawn from it are, that either the phosphates in the water are not originally derived from an organic source, or, if they are, that large quantities of water must have passed through the strata in which these organic remains were deposited, and thus have washed away the more soluble nitrates from amongst them. This, I believe, is really what has taken place.

Before forming an opinion myself of the source of the deep well-water in the chalk, I thought it was necessary to examine, if possible, the water from the different strata which form the London Basin; and for this purpose I procured what I was told was a specimen of water from the plastic clay or tertiary strata, and from that part of the strata which immediately overlies the chalk. I did not make a full analysis, but only estimated certain substances in it; my results, however, showed this water to have a great similarity in many respects to the deep well-water, but they differed so much from analyses already published upon the water, that I thought perhaps I might not have had a genuine specimen given to me; and as it is a point too intimately connected with this subject to be entirely passed over, I deferred proceeding further until I had a little more leisure, and until I could procure and examine other specimens, and, if possible, from wells in the strata in different localities, when I hope, with the kind permission of the Society, again to bring the subject before their notice.

* Chem. Soc. Mem. ii. 392.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

January 21, 1856.

The MASTER of the MINT, Vice-President, in the Chair.

The following donations were announced:—

“The Journal of the Society of Arts:” from the Society.

“The Journal of the Photographic Society:” from the Society.

“The Literary Gazette:” from the Publishers.

“The Pharmaceutical Journal:” from the Editor.

“The Journal of the Franklin Institute:” from the Institute.

“The American Journal of Science and Art:” from the Editors.

“On the Action of Water upon certain Sulphomethylates:” by A. H. Church. From the Author.

“On the Spontaneous Decomposition of certain Sulphomethylates:” by A. H. Church. From the Author.

Dr. H. E. Roscoe was elected a Fellow of the Society.

Dr. W. A. Miller delivered a discourse “On some points in the practice of the Assay of Gold and Silver.”

February 4, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

“Elements of Chemistry, Theoretical and Practical,” Second Part: by Dr. W. A. Miller. From the Author.

“Report of the Commission appointed to make Inquiries into

the state of the Manufacture of Iron and Brass Ordnance:" from F. A. Abel.

"The Journal of the Society of Arts:" from the Society.

"The Journal of the Photographic Society:" from the Society.

"The Literary Gazette:" from the Publishers.

"The Pharmaceutical Journal:" from the Editor.

"The Memoirs and Proceedings of the Academy of Sciences of Madrid, for the years 1851, 1852, and 1853:" from the Academy.

The following papers were read:—

"Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre:" by F. A. Abel and C. L. Bloxam.

"Note on the Solubility of Sulphate of Baryta in Hydrochloric Acid:" by Henry M. Noad, Ph.D.

Dr. A. W. Hofmann made a verbal communication "On a New Class of Alcohols."

February 18, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.

"The Journal of the Society of Arts:" from the Society.

"The Journal of the Franklin Institute:" from the Institute.

"The Report of the Council of the Art-Union of London for 1856:" from the Art-Union.

"The Almanack of the Art-Union of London for 1856:" from the Art-Union.

"On the supposed Influence of the Hot-Blast in augmenting the quantity of Phosphorus in Pig-Iron:" by David S. Price, Ph.D., and Edward Chambers Nicholson. From the Authors.

Nathan Mercer, Esq., of Liverpool, was elected a Fellow of the Society.

Dr. A. W. Hofmann delivered a discourse "On some New Bases containing Phosphorus."

March 3, 1856.

Dr. A. W. WILLIAMSON, Vice-President, in the Chair.

The following donations were announced:—

- “The Literary Gazette:” from the Publishers.
- “The Journal of the Photographic Society:” from the Society.
- “The Journal of the Society of Arts:” from the Society.
- “The Pharmaceutical Journal:” from the Editor.

The following gentlemen were elected Fellows of the Society:—

G. C. Foster, B.A., University College, London.

Arthur Herbert Church, Esq., 9, Bedford Row, Gray's Inn.

Augustus Beauchamp Northcote, Esq., 37, Argyle Square.

The following papers were read:—

“On the Source of the Water of the deep Wells in the Chalk under London:” by Dugald Campbell.

“On the Action of Chloride of Cyanogen on Naphthalamine:” by William H. Perkin.

“On some New Colouring Matters, Derivatives of Dinitrobenzole, Dinitronaphthaline, &c. :” by A. H. Church and W. H. Perkin.

March 17, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

- “The Literary Gazette:” from the Publishers.
- “The Journal of the Society of Arts:” from the Society.
- “The Journal of the Franklin Institute:” from the Institute.
- “Bericht der kaiserlichen Akademie der Wissenschaften zu Wien:” from the Academy.

Dr. J. H. Gladstone delivered a discourse “On some Laws of Chemical Combination.”

ANNIVERSARY MEETING,

March 31, 1856.

Dr. W. A. MILLER, President, in the Chair.

The Report of the Council, and the Audited Account of the Treasurer, were read.

It was Resolved,—

“That in By-Law 2, ‘Of Honorary and Foreign Members,’ the first sentence of the second paragraph be altered, and in future stand as follows:—‘The number of Foreign Members shall not exceed twenty-five.’”

Mr. W. Ferguson and Mr. A. B. Northcote having been appointed Scrutators, the meeting proceeded to the election of Council and Officers for the ensuing year, and the following gentlemen were declared to have been duly elected:—

PRESIDENT.

W. A. Miller, M.D., F.R.S.

VICE-PRESIDENTS

(WHO HAVE FILLED THE OFFICE OF PRESIDENT).

| | |
|---------------------------------|------------------------------|
| W. T. Brande, F.R.S. | Thomas Graham, F.R.S. |
| C. G. B. Daubeney, M.D., F.R.S. | Colonel Philip Yorke, F.R.S. |

VICE-PRESIDENTS.

| | |
|---------------------------------|---------------------------------|
| B. C. Brodie, F.R.S. | G. D. Longstaff, M.D. |
| Warren De la Rue, Ph.D., F.R.S. | A. W. Williamson, Ph.D., F.R.S. |

SECRETARIES.

| | |
|---------------------------|----------------------|
| Theophilus Redwood, Ph.D. | William Odling, M.B. |
|---------------------------|----------------------|

FOREIGN SECRETARY.

A. W. Hofmann, Ph.D., F.R.S.

TREASURER.

Robert Porrett, F.R.S.

OTHER MEMBERS OF THE COUNCIL.

| | |
|---------------------------|-------------------------------|
| F. A. Abel, Esq. | William Herapath, Esq. |
| C. L. Bloxam, Esq. | Charles Heisch, Esq. |
| G. B. Buckton, Esq. | H. Bence Jones, M.D., F.R.S. |
| Dugald Campbell, Esq. | Hugh Lee Pattinson, F.R.S. |
| J. H. Gilbert, Ph.D. | John Stenhouse, LL.D., F.R.S. |
| W. C. Henry, M.D., F.R.S. | John Thomas Way, Esq. |

It was moved by Dr. A. W. Williamson, seconded by Robert Porrett, Esq., and Resolved,—

“That Professor Benjamin Collins Brodie having resigned the office of Secretary, this meeting desires to express their regret at the loss of his services, and request the President to convey to him, in the form he may think most suitable, their thanks for the zeal he has manifested in promoting the interests of the Chemical Society; and, at the same time, to congratulate him on the more extensive sphere of action to which he has lately been appointed.”

The thanks of the meeting were voted to the President, Officers, and Council, for their services during the past year.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.

BY HENRY WATTS, B.A., F.C.S.

**Chemical Report on the Mode of Detecting Vegetable Substances
mixed with Coffee for the purpose of Adulteration.**

By T. Graham, F.R.S., J. Stenhouse, F.R.S., and D. Campbell, F.C.S.

THE adulteration of coffee in the condition of the original bean, unground and unroasted, could only be effected by the substitution of a different seed, and would form the subject of an inquiry entirely botanical. But it is proper to remark that the coffee-bean is liable to be rendered entirely worthless, without any injury to its structure, when kept in a wet or damp state for some time,—apparently from the readiness with which the soluble constituents of the bean spontaneously ferment. Coffee damaged by sea-water has been found to retain neither the aroma nor bitter flavour of the seed, and to have lost the whole of its characteristic principle, caffeine. The entire soluble matter which can be extracted from the damaged seeds by boiling water is greatly reduced, and does not exceed 12 per cent. of their weight, while the presence of the salts of sea-water is always sufficiently obvious.

The coffee-bean, in its fresh, unprepared state, is tough, and ground with difficulty. It yields an infusion without aroma, which is bitter, and is said to act more powerfully on the nerves than roasted coffee. This seed, however, is always roasted before being made use of, and it is in that state, and with its structure more or less obliterated by grinding, that it must be identified, and its purity established by chemical means of investigation.

In consequence of torrefaction, coffee is materially altered, and acquires new properties. The woody tissue of the fresh bean is

horny, and differs from ordinary woody fibre in its composition, and is also said not to yield sugar when treated with sulphuric acid. By the roasting, this woody tissue undergoes a partial decomposition, and becomes friable, and the difficulty of pulverising the seed, and exhausting it by water, is removed. There is produced at the same time a soluble brown bitter matter, due in part to a gummy substance pre-existing in the coffee, altered like starch by torrefaction, but principally to the conversion into caramel of a quantity of sugar in the coffee-bean, amounting to 6 or 7 per cent. of its weight.

A still more characteristic product of the roasting of coffee, is that which gives it aroma. This principle, when separated from the infusion of coffee by distillation, is found to be a brown liquid oil, heavier than water, soluble in ether, and has received the name of *Caffeone* (Boutron and Frémy). Caffeone is slightly soluble in boiling water; a quantity of caffeone which is almost insensible will aromatise two or three pints of water.

In common with all the valuable constituents of coffee, caffeone is found to come from the soluble portion of the roasted seed.

The caffeic acid of the green coffee is also changed by the roasting into an acid of different properties.

Of the crystallisable caffeine, a small portion may be lost from its volatility in roasting.

No seed appears to be known, which, roasted and pulverised, forms a true equivalent and sufficient substitute for coffee, either in the physiological properties or chemical composition of its soluble extract. A great variety of seeds were tried in France, as substitutes for coffee, during the continuance of the Continental blockade, including, in addition to maize, barley, oats, and the other cereals, the seeds of the yellow flag (*Iris pseudo-acorus*), grey pea (*Cicer arietinum*), the milk vetch, or Andalusian astragalus (*Astragalus boeticus*), the *Hibiscus esculentus*, holly, Spanish broom, acorns, chesnuts, the small lupin (*Lupinus angustifolia*), peas, haricots, horse-beans, sunflower, pips of the gooseberry and grape, eglantine (*Rosa villosa*), and the capsules of box (*Buxus sempervirens*). Of the seeds enumerated, the yellow flag, a common marsh plant in England, appears to have offered the only similarity to coffee; but it is doubtful whether the resemblance extended beyond the aroma of this seed when roasted, which is certainly suggestive of coffee.

The search made among the seeds of other plants for a substitute for the coffee-berry may then be said to have entirely failed.

The divergence of the root-substitutes from true coffee is still greater in every property except one. The roots which have been most used are those of chicory (*Cichorium intybus*), carrot,

beet, rush-nut (*Cyperus esculentus*), earth-nut (*Arachis hypogæa*), scratch-weed (*Gallium aparine*), fern (*Polypodium filix mas*), and butchers' broom (*Ruscus aculeatus*).

The roots of chicory, and of beet and carrot, which are all extensively used in Germany, are similarly prepared, being cut into thin slices, dried in a stove, and then passed through a coffee-roaster,—generally with the addition of about 2 per cent. of butter, and sometimes of a red powder, to give the colour of coffee.

It is to be remarked of the roots, that they are generally used rather as an addition to coffee than as a substitute for it. In one property these roots all agree, and we have no doubt that it has led to this common application of them: chicory, beet, carrot, &c., are all remarkable for containing a large quantity of sugar, easily caramelised by heat. They acquire, when roasted, the bitter of burnt sugar, with a somewhat similar aroma. Now the taste of this bitter appears to be one of the strongest and most general of our gustatory preferences. It equally recommends toast-water, and the varieties of brown beer or porter, in the preparation of which a portion of malt is used with its sugar caramelised by heat. The caramel bitter is, in fact, a stock flavour, which we find modified by the most various accessories in different beverages, and even in solid articles of diet in a cooked state. It is not surprising, therefore, that the chicory root, containing as it does about 30 per cent. of sugar, more than one-half of which is caramelised in roasting, should obtain extensive favour as an addition to coffee. Fresh chicory has a certain bitterness, or rather acidity, but this is overpowered in the torrefied root by the caramel bitter, and this root may be adequately replaced by the bland beet or carrot similarly prepared. No one of these roots contains any constituent which associates it with coffee, except sugar:—in other respects they are entirely different.

The preparation of roasted chicory appears to have originated in Holland upwards of a century ago, but remained secret till 1801. It is now prepared on a great scale, both on the Continent and in England. The quantity of chicory-powder consumed annually in France is known to amount 6,000,000 kilogrammes.

In the chemical examination of ground coffee, with the view to discover if it is mixed with the vegetable substances which have been named, or with others, the characteristic constituents of the coffee are less immediately available than certain properties of the infusion of a physical character. This arises from the circumstance, that although it is easy to discover the presence of caffeic acid and caffeine, yet the determination of the exact quantity of these substances in an infusion is both difficult and tedious.

There is reason also to believe that the proportion of caffeic acid

and caffeine varies considerably in different samples of coffee, so that the quantities of these substances (when found) could not show exactly the proportion of pure coffee in a mixture. It will be most advantageous to discuss here the general properties of the coffee infusion, in the first instance, as they are most easily observed; and a single character of this kind in some instances, and two or three in others, will generally be sufficient to establish adulteration when it has been practised. The higher chemical inquiries will then follow.

1. When hot water is applied to the powder of chicory and other roots, it softens immediately, from the facility with which water is imbibed, while the grains of coffee remain hard and gritty in the same circumstances. Ground chicory is highly hygroscopic.

Roasted grain, such as wheat and barley, gives an infusion with hot water, which is mucilaginous and thick, while the infusion of coffee is remarkably thin and limpid. The grain infusion generally contains starch, and gives, when cool, a blue colouration with iodine, while the infusions of both coffee and chicory appear to be entirely destitute of starch.

2. The more deep and rapid coloration of water by chicory and the allied roots than by coffee, affords a useful indication in a preliminary examination. The roasted grains also appear to colour water more deeply than coffee does. The relative colouring power of coffee, chicory, and a variety of other vegetable substances used in the adulteration of coffee, was determined with considerable precision by infusing equal quantities of each in water, as in the preparation of coffee, filtering the infusions through paper, and observing the colour in glass tubes of equal diameter—about 1 inch. The solutions required to be very dilute. It was also necessary to have a standard of comparison, and for this purpose caramel, carefully prepared from cane-sugar, was had recourse to. The standard solution of caramel consisted of 1 grain of that substance dissolved in 2000 grains of water. To produce the same intensity of colour as the standard solution, a larger proportion than 1 grain of all the other substances required to be dissolved in 2000 grains of water. The proportion necessary is expressed in Table I. The substances are all roasted, as they would be used to mix with coffee.

TABLE I.

Weight of substance (roasted) dissolved in 2000 parts of water, to produce an equal depth of colour.

| | |
|---------------------------------------|-------|
| Caramel | 1. |
| Mangold-wurzel | 1.66 |
| Bouka (a coffee substitute) | 1.66 |
| Sparke's vinegar colouring | 1.74 |
| Black malt | 1.82 |
| White turnips | 2.0 |
| Carrots | 2.0 |
| Chicory (darkest Yorkshire) | 2.22 |
| Parsnips | 2.5 |
| Maize | 2.86 |
| Rye | 2.86 |
| Dandelion root | 3.33 |
| Red beet | 3.33 |
| Bread raspings | 3.64 |
| Acorns | 5.00 |
| Over-roasted coffee | 5.46 |
| Highly-roasted coffee | 5.77 |
| Medium-roasted coffee | 6.95 |
| Another specimen of coffee | 6.66 |
| White lupin seed | 10.00 |
| Peas | 13.33 |
| Beans | 13.33 |
| Spent tan | 33. |
| Brown malt | 40. |

It will be seen from the preceding table, that 2.22 parts of chicory have the same colouring power as 5.77 grains of highly-roasted, and 6.95 grains of medium-roasted coffee, or of 13.33 grains of roasted peas, and 40 parts of brown malt.

The same results are given in a different form in Table II.

TABLE II.

Colouring power of various substances (roasted) dissolved in an equal quantity of water.

| | |
|---------------------------------------|--------|
| Caramel | 1000. |
| Mangold-wurzel | 602.4 |
| Bouka (a coffee substitute) | 602.4 |
| Sparke's vinegar colouring | 574.71 |
| Black malt | 549.45 |
| White turnips | 500. |
| Carrots | 500. |
| Chicory (darkest Yorkshire) | 450.45 |

| | |
|--------------------------------------|--------|
| Parsnips | 400· |
| Maize | 350· |
| Rye | 350· |
| Dandelion root | 300·3 |
| Red beet | 300·3 |
| Bread raspings | 274·72 |
| Acorns | 200· |
| Over-roasted coffee | 183·15 |
| Highly-roasted coffee | 173·31 |
| Medium-roasted coffee | 143·88 |
| Another specimen of coffee | 150·15 |
| White lupin seed | 100· |
| Peas | 73·18 |
| Beans | 75·18 |
| Spent tan | 30· |
| Brown malt | 25· |

The number for chicory (450) indicates that that substance possesses nearly half the colouring power of caramel (1000); while highly-roasted coffee (173) is about one-sixth of caramel. Maize and rye, with probably all the other cereals, rise to 350, and have therefore a high colouring power, quite double that of coffee; while peas and beans (75) are on the other side, and possess only about half the colouring power of coffee for equal weights of the substances compared.

The preceding solutions were prepared at 212°, and chicory then exhibits about three times the colouring power of coffee. But when the solutions are prepared without heat, the disparity is still greater. In cold water chicory exceeded coffee about four and a half times in colouring power.

When a few grains of roasted chicory, or any other sweet root, are dropped into a glass of cold water, without being stirred, a yellowish-brown colour diffuses rapidly through the liquid, while the pure coffee gives no sensible colour to the water in similar circumstances.

3. Another property of infusions, which is still more precise and valuable, is their specific gravity.

The proportion of substance found most suitable for an extensive comparison was 1 in 10 of water. The substances were not exhausted by water, but simply placed in about a pint of cold water, in the preceding proportion by weight, and the temperature raised to 212°, and retained at that point for not more than half a minute. The infusions were then filtered through paper. The substances, as usual, are roasted and ground equally fine, with the exception of the last three in the table.

TABLE III.

Specific gravity of solutions at 60° F., 1 part of substance to
10 parts of water.

| | |
|---------------------------------------|---------|
| Spent tan | 1002·14 |
| Lupin seed | 1005·7 |
| Acorns | 1007·3 |
| Peas | 1007·3 |
| Mocha coffee | 1008·0 |
| Beans | 1008·4 |
| Neilgherry coffee | 1008·4 |
| Plantation Ceylon coffee | 1008·7 |
| Java coffee | 1008·7 |
| Jamaica coffee | 1008·7 |
| Costa Rica coffee | 1008·98 |
| Native Ceylon coffee | 1009·0 |
| Costa Rica coffee | 1009·5 |
| Brown malt | 1010·9 |
| Parsnips | 1014·3 |
| Carrots | 1017·1 |
| Bouka | 1018·5 |
| English chicory (Yorkshire) | 1019·1 |
| Black malt | 1021·2 |
| Turnips | 1021·4 |
| Rye meal | 1021·6 |
| English chicory | 1021·7 |
| Dandelion root | 1021·9 |
| Red beet | 1022·1 |
| Foreign chicory | 1022·6 |
| Guernsey chicory | 1023·2 |
| Mangold-wurzel | 1023·5 |
| Maize | 1025·3 |
| Bread raspings | 1026·3 |
| British gum | 1037·9 |
| Gum arabic | 1038·6 |
| Cane sugar | 1040·9 |
| Starch sugar | 1042·8 |

The leguminous seeds, it appears, give a low specific gravity,—peas 1007·3, and beans 1008·4. The coffees are also remarkably low, varying from Mocha coffee 1008·0, to Costa Rica 1009·5; while chicory rises greatly, ranging in different samples between 1019·1 and 1023·2. The cereals are equally high, or still higher, in the scale of gravity; rye-meal being 1021·6, and maize 1025·3. The low gravity of the coffee infusion, therefore, distinguishes it sharply from the two most important classes of adulterating substances,—the roots and cereals.

4. The action of other solvents, besides water, may be shortly referred to.

Agitated four times successively in ten times their weight of ether, the substances to be mentioned gave different proportions of matter soluble in that menstruum:—

| | | |
|-------------------------|-------|-----------------------------|
| Roasted beans . . . | 1.81 | per cent. of oil and resin, |
| „ maize . . . | 5.15 | „ „ „ |
| „ chicory (Yorkshire) . | 6.83 | „ „ „ |
| „ coffee (Mocha) . | 15.93 | „ „ „ |

including probably nearly 1 per cent. of caffeine.

It thus appears that coffee yields much more soluble matter to ether than beans, maize, or chicory, which represent the three classes of leguminous seeds, cereals, and sweet roots. The fat obtained from chicory was no doubt principally composed of the sweet American or Australian tallow, added by English manufacturers to the root, in roasting, to prevent burning. The experiment with ether is easily made, and may in particular circumstances prove valuable.

The solubility of the same substances in proof spirit was observed, the substance being exhausted four times in succession by ten times its weight of proof spirit, at the boiling temperature.

Roasted beans gave 17.5 per cent. of a dry, blackish, lustrous extract.

Roasted maize gave 50.2 per cent. of an extract much like the preceding.

Roasted chicory (Yorkshire) gave 67.76 per cent. of extract of a lighter colour than the preceding, but otherwise very similar.

Roasted coffee (Mocha) gave 26.35 per cent. of extract, much like the first two in external appearance.

These operations are remarkably tedious, while the experiments with ether, on the contrary, are easy and simple. The results with proof spirit are not sufficiently characteristic to recommend its application.

5. Fermentation by means of yeast gives a decisive proof of the adulteration of coffee by many vegetable substances, particularly by chicory and the other saccharine roots.

In our fermentation experiments, 2000 grains of the coffee or other substances were weighed out, and treated successively with $1\frac{1}{2}$ pint of cold water, $1\frac{1}{2}$ pint of water about 174° , and a little additional water for washing the solid residue upon a filter of fine calico. About 3 pints of infusion were thus obtained, which were mixed with 250 grains of brewers' yeast, weighed after being pressed in a calico bag. The fermentation was continued for forty-eight hours at a temperature of from 80° to 90° . The fermented liquor was afterwards distilled, and about 6000 grains

brought over. The last vinous liquor was rectified a second time, about 3000 grains being now collected; and the alcohol was inferred from the density of this distillate.

The substances were examined for sugar both before and after being roasted, as it was interesting to observe the extent to which the sugar is caramelised, by torrefaction, in the different substances.

The sugar of coffee is found to be reduced by roasting from 6 to 7 per cent. in raw coffee, to from 0· to 1·12 per cent. in the roasted,—or to be almost entirely destroyed; while in other substances the sugar is more generally reduced, by precisely similar treatment, to from one-half to one-third of its original proportion. It is difficult to account for this dissimilarity, unless a portion of the sugar of raw coffee exists in a state of conjugate combination, like the sugar in tannin, amygdalin, salicin, &c.: our attempts to isolate such a conjugate body, however, from raw coffee, have not yet proved successful, and its existence is therefore hypothetical. We succeeded, on the other hand, in crystallising out cane-sugar from an infusion of raw coffee. It was decided by proper experiments that the fermentation of sugar was not interfered with by the empyreumatic products, or essential oil of roasted coffee.

The sugar was determined which exists in the most dissimilar varieties of coffee, the wild and cultivated beans, the beans from Ceylon and the West Indies, from Arabia, and the Neilgherry Hills. Twelve different samples were examined, each both before and after roasting.

TABLE IV.

Sugar found in coffee, before and after torrefaction.

| | | | | Sugar per Cent. | |
|-----|-------------------|---|---|-----------------|----------|
| | | | | Raw. | Roasted. |
| 1. | Plantation Ceylon | . | . | 7·52 | 1·14 |
| 2. | „ „ | . | . | 7·48 | 0·63 |
| 3. | „ „ | . | . | 7·70 | 0·0 |
| 4. | „ „ | . | . | 7·10 | 0·0 |
| 5. | Native Ceylon | . | . | 5·70 | 0·46 |
| 6. | Java | . | . | 6·73 | 0·48 |
| 7. | Costa Rica | . | . | 6·72 | 0·49 |
| 8. | „ „ | . | . | 6·87 | 0·40 |
| 9. | Jamaica | . | . | 7·78 | 0·0 |
| 10. | Mocha | . | . | 7·40 | 0·50 |
| 11. | „ | . | . | 6·40 | 0·0 |
| 12. | Neilgherry | . | . | 6·20 | 0·0 |

The sugar in coffee appears to be increased by cultivation,—the proportion in Native Ceylon being 5·7 per cent., and in Plantation Ceylon from 7·1 to 7·7 per cent.

The proportion of sugar in the dried roots is high at first, and continues after roasting still very notable.

TABLE V.
Sugar in chicory and other sweet roots, before and after torrefaction.

| | Sugar per Cent. | |
|-----------------------------------|-----------------|----------|
| | Raw. | Roasted. |
| Foreign chicory . . . | 23·76 | 11·98 |
| Guernsey chicory . . . | 30·49 | 15·96 |
| English chicory . . . | 35·23 | 17·98 |
| „ „ (Yorkshire) . . . | 32·06 | 9·86 |
| Mangold-wurzel . . . | 23·68 | 9·96 |
| Carrots (ordinary) . . . | 31·98 | 11·53 |
| Turnips „ . . . | 30·48 | 9·65 |
| Beet root (red) . . . | 24·06 | 17·24 |
| Dandelion root . . . | 21·96 | 9·08 |
| Parsnips . . . | 21·70 | 6·98 |
| Bouka (a coffee substitute) . . . | — | 5·82 |

It thus appears that roasted chicory, as it is sold for mixing with coffee, retains from 9·86 to 17·98 per cent. of undecomposed sugar. In none of the other sweet roots which are occasionally substituted for chicory, such as mangold-wurzel, beet, turnip, or carrot, does the proportion of sugar retained after torrefaction fall under 9 per cent., with the exception of parsnip, in which the sugar falls to 6·98 per cent. The coffee substitute, “Bouka,” falls into this class, and appears to be a mixture of true coffee with a torrefied sweet root.

The last group is composed of the leguminous and certain other seeds, with the cereals. The sugar was determined for most of these substances in the roasted form of the grain only, which alone affects the question of adulteration.

TABLE VI.
Sugar in various seeds, before and after torrefaction.

| | Sugar per Cent. | |
|----------------------|-----------------|----------|
| | Raw. | Roasted. |
| Acorns . . . | 3·64 | 2·70 |
| Horse-beans . . . | — | 1·62 |
| Peas (grey) . . . | — | 1·08 |
| Maize . . . | — | 0·82 |
| Rye-meal . . . | — | 1·96 |
| Bread-raspings . . . | — | 1·78 |
| Lupin-seed . . . | — | 0·74 |
| Brown malt . . . | 8·48 | — |
| Black malt . . . | — | 1·66 |

In the roasted seeds enumerated, the proportion of sugar is sensible, but not sufficiently considerable to give the means of distinguishing leguminous seeds and cereals from coffee. In roasted acorns, the sugar rises to 2·7 per cent., and black malt, it will be observed, still retains 1·66 per cent. of fermentable matter.

The fermentation test, on the other hand, is adapted to detect adulteration by chicory and the sweet roots, and will, we believe, from its certainty and facility of application, prove eminently useful for that purpose.

6. Coffee, and the various vegetable substances used in its adulteration, may be incinerated on a platinum or porcelain capsule, and leave an earthy ash, of which the composition is often characteristic of the plant. Valuable information may be obtained, without making a formal analysis of the ash, by simply digesting it in strong hydrochloric acid. The earth which remains undissolved after this treatment is silica. Now coffee, we find, is remarkably distinguished from the roots and cereals, by the small quantity of silica it affords. The quantity of that earth found in coffee is so small, that it may be doubted whether coffee contains any silica except what may accidentally adhere to the coffee beans, when collected, in the form of sand. The proportion of silica found in the twelve samples of coffee of Table IV. was as follows:—

TABLE VII.
Silica in roasted coffee.

| Sample | 1 | . | . | . | Per Cent. in Ash. |
|--------|----|---|---|---|-------------------|
| | 1 | . | . | . | 0· |
| „ | 2 | . | . | . | 0· |
| „ | 3 | . | . | . | 0·26 |
| „ | 4 | . | . | . | 0·02 |
| „ | 5 | . | . | . | 0·17 |
| „ | 6 | . | . | . | 0·28 |
| „ | 7 | . | . | . | 0· |
| „ | 8 | . | . | . | 0·45 |
| „ | 9 | . | . | . | 0· |
| „ | 10 | . | . | . | 0· |
| „ | 11 | . | . | . | 0· |
| „ | 12 | . | . | . | 0·09 |

The only case in which the silica approaches to half a per cent. of the ash is Sample 8; and in another sample of the same coffee, which was properly screened before roasting, the silica of the ash fell to 0.

On the other hand, the silica and sand, insoluble in acids, of four samples of roasted chicory, amounted to so much as 10·69,

13·13, 30·71, and 35·85 per cent. of the ash. It may be added, that the portion of this silica soluble in alkali was, in the same samples, 2·61, 3·81, 10·52, and 12·75 parts; the portion of silica insoluble in alkali, 8·08, 9·32, 20·19, and 23·10 parts.

The whole silica in roasted dandelion root amounted to 11·26 per cent. of the ash.

In other cultivated roots the proportion of silica does not appear to be so large as in chicory. The silica is always expressed with reference to 100 parts of the ash. Messrs. Way and Ogston find in the root of the carrot from 0·76 to 1·92 silica; in beet, from 1·4 to 4·11 silica; and in turnip, from 0·96 to 2·75 silica.

The proportion of silica appears to be low in certain grains and seeds, although rarely descending to the insignificant proportion of the coffee-bean,—and to be very high in other grains. We find in the ashes of acorns 1·01 per cent. of silica; in maize, 1·78 per cent. of silica; in the white lupin of the Levant, 0·87 per cent. of silica. Messrs. Ogston and Way report from 2·05 to 5·46 silica for wheat; from 23·6 to 70·77 silica for barley; from 38·48 to 50·03 for oats; and 9·22 for rye.

It appears, therefore, that the presence of 1 per cent. or upwards of silica in the ashes of coffee is a proof of adulteration; that the adulterating substances which increase the proportion of silica most considerably are oats and barley, then chicory and dandelion, which are followed by rye: wheat, beet, turnip, and carrot, would produce a small and less decisive effect.

There will now be presented complete analyses, made for this inquiry, of the ashes of seven varieties of coffee, and four different samples of chicory.

TABLE VIII.
Analyses of the ashes of coffee and chicory.

COFFEE.

| | Plant- ation Ceylon | Native Ceylon | Java. | Costa Rica. | Ja- maica. | Mocha. | Neil- gherry. |
|-------------------------------|---------------------------|------------------|-------|----------------|---------------|--------|------------------|
| Potash | 55·10 | 52·72 | 54·00 | 53·20 | 53·72 | 51·52 | 55·80 |
| Soda | — | — | — | — | — | — | — |
| Lime | 4·10 | 4·58 | 4·11 | 4·61 | 6·16 | 5·87 | 5·68 |
| Magnesia | 8·42 | 8·46 | 8·20 | 8·66 | 8·37 | 8·87 | 8·49 |
| Sesquioxide of iron | 0·45 | 0·98 | 0·73 | 0·63 | 0·44 | 0·44 | 0·61 |
| Sulphuric acid | 3·62 | 4·48 | 3·49 | 3·82 | 3·10 | 5·26 | 3·09 |
| Chlorine | 1·11 | 0·45 | 0·26 | 1·00 | 0·72 | 0·59 | 0·60 |
| Carbonic acid | 17·47 | 16·93 | 18·13 | 16·34 | 16·54 | 16·98 | 14·92 |
| Phosphoric acid | 10·36 | 11·60 | 11·05 | 10·80 | 11·13 | 10·15 | 10·85 |
| Silica | — | — | — | — | — | — | — |
| Sand | — | — | — | — | — | — | — |
| Total amount | 100·63 | 100·20 | 99·97 | 99·06 | 100·18 | 99·68 | 100·04 |

CHICORY.

DEDUCTING SAND AND SILICA.

| | Darkest English (Yorkshire) | English. | Foreign. | Guernsey. |
|-------------------------------|-----------------------------------|----------|----------|-----------|
| Potash | 38·53 | 27·85 | 46·07 | 46·27 |
| Soda | 9·34 | 16·90 | 3·17 | 5·49 |
| Lime | 10·79 | 10·81 | 7·78 | 7·65 |
| Magnesia | 6·06 | 8·08 | 5·33 | 5·55 |
| Sesquioxide of iron | 4·38 | 3·50 | 8·29 | 5·08 |
| Sulphuric acid | 11·38 | 11·78 | 8·38 | 8·67 |
| Chlorine | 5·67 | 5·23 | 5·03 | 6·58 |
| Carbonic acid | 2·04 | 3·22 | 4·36 | 4·60 |
| Phosphoric acid | 12·27 | 12·61 | 11·00 | 9·59 |
| Silica | — | — | — | — |
| Sand | — | — | — | — |
| Total amount | 100·46 | 99·98 | 99·41 | 99·48 |

DEDUCTING SAND AND NOT SILICA.

| | Darkest English (Yorkshire) | English. | Foreign. | Guernsey. |
|-------------------------------|-----------------------------------|----------|----------|-----------|
| Potash | 37·07 | 27·13 | 40·20 | 41·41 |
| Soda | 8·99 | 16·46 | 2·77 | 4·92 |
| Lime | 10·38 | 10·53 | 6·79 | 6·85 |
| Magnesia | 5·83 | 7·87 | 4·66 | 4·97 |
| Sesquioxide of iron | 4·22 | 3·41 | 7·24 | 4·55 |
| Sulphuric acid | 10·95 | 11·48 | 7·32 | 7·76 |
| Chlorine | 5·46 | 5·10 | 4·39 | 5·89 |
| Carbonic acid | 1·97 | 3·14 | 3·81 | 4·12 |
| Phosphoric acid | 11·81 | 12·29 | 9·60 | 8·59 |
| Silica | 3·81 | 2·61 | 12·75 | 10·52 |
| Sand | — | — | — | — |
| Total amount | 100·49 | 100·02 | 99·53 | 99·58 |

NOT DEDUCTING SAND AND SILICA.

| | Darkest English (Yorkshire) | English. | Foreign. | Guernsey. |
|-------------------------------|-----------------------------------|----------|----------|-----------|
| Potash | 33·48 | 24·88 | 29·56 | 32·07 |
| Soda | 8·12 | 15·10 | 2·04 | 3·81 |
| Lime | 9·38 | 9·60 | 5·00 | 5·31 |
| Magnesia | 5·27 | 7·22 | 3·42 | 3·85 |
| Sesquioxide of iron | 3·81 | 3·13 | 5·32 | 3·52 |
| Sulphuric acid | 10·29 | 10·53 | 5·38 | 6·01 |
| Chlorine | 4·93 | 4·68 | 3·23 | 4·56 |
| Carbonic acid | 1·78 | 2·88 | 2·80 | 3·19 |
| Phosphoric acid | 10·66 | 11·27 | 7·06 | 6·65 |
| Silica | 3·81 | 2·61 | 12·75 | 10·52 |
| Sand | 9·32 | 8·08 | 23·10 | 20·19 |
| Total amount | 100·85 | 99·98 | 100·66 | 99·68 |

The first difference which appears upon comparing the two sets of analyses is the absence of soda in coffee, and its presence in chicory to the extent of from 2·04 to 15·1 per cent. of the ash. The united amount of potash and soda does not differ much in the two substances. In chicory, the lime is greater and the magnesia less than in coffee. The sesquioxide of iron is strikingly different, being always under 1 per cent. in coffee, by our experiments, and ranging from 3·13 to 5·32 per cent. in chicory. The ash of chicory is, on this account, red to the eye when compared with that of coffee. The difference in chlorine is also important, the highest proportion observed in coffee-ash being 1·11 per cent., and the lowest proportion in chicory-ash 3·28 per cent. Coffee gives an ash which is highly carbonated, the carbonic acid varying from 14·92 to 18·13 per cent.; while the ash of chicory is only slightly carbonated, containing from 1·78 to 3·19 per cent. of carbonic acid. The proportion of phosphoric acid is pretty similar in the two kinds of ash. The disparity in the silica has been already referred to.

The differences most available in the two kinds of ash, as distinctive tests for coffee and chicory, appear to be the following:—

| | In coffee-ash. | In chicory-ash. |
|-------------------------------|----------------|-----------------|
| Silica and sand | — | 10·69 to 35·85 |
| Carbonic acid | 14·92 to 18·13 | 1·78 to 3·19 |
| Sesquioxide of iron | 0·44 to 0·98 | 3·13 to 5·32 |
| Chlorine | 0·26 to 1·11 | 3·28 to 4·93 |

Another series of ash analyses was executed, comprising the ash of the white lupin of the Levant—a seed which, from its chemical properties and low price, is not unlikely to be substituted for coffee—the ash of acorns, of maize, and of parsnip and dandelion roots.

TABLE IX.
Analyses of ashes of certain seeds and roots,
DEDUCTING SILICA, &c.

| | Lupins. | Acorns. | Maize. | Parsnips. | Dandelion root. |
|-------------------------------|---------|---------|--------|-----------|-----------------|
| Potash | 33·83 | 55·49 | 31·28 | 56·86 | 20·22 |
| Soda | 17·90 | 0·63 | — | — | 34·87 |
| Lime | 7·81 | 6·98 | 3·11 | 6·88 | 12·87 |
| Magnesia | 6·23 | 4·36 | 14·98 | 6·52 | 1·47 |
| Sesquioxide of iron | — | 0·54 | 0·85 | 0·53 | 1·42 |
| Chlorine | 2·12 | 2·53 | 0·50 | 2·10 | 4·32 |
| Sulphuric acid | 6·85 | 4·83 | 4·20 | 4·09 | 2·66 |
| Carbonic acid | 0·56 | 13·82 | — | 11·50 | 6·99 |
| Phosphoric acid | 25·74 | 11·26 | 45·29 | 13·91 | 12·63 |
| Silica, &c. | — | — | — | — | — |
| Total amount | 101·04 | 100·44 | 100·21 | 102·39 | 97·45 |

Analyses of ashes of certain seeds and roots,

NOT DEDUCTING SILICA, &c.

| | Lupins. | Acorns. | Maize. | Parsnips. | Dandelion root. |
|-------------------------------|---------|---------|--------|-----------|-----------------|
| Potash | 33·54 | 54·93 | 30·74 | 56·54 | 17·95 |
| Soda | 17·75 | 0·63 | — | — | 30·95 |
| Lime | 7·75 | 6·01 | 3·06 | 6·85 | 11·43 |
| Magnesia | 6·18 | 4·32 | 14·72 | 6·49 | 1·31 |
| Sesquioxide of iron | — | 0·54 | 0·84 | 0·53 | 1·27 |
| Chlorine | 2·11 | 2·51 | 0·50 | 2·09 | 3·84 |
| Sulphuric acid | 6·80 | 4·79 | 4·13 | 4·07 | 2·37 |
| Carbonic acid | 0·56 | 13·69 | — | 11·44 | 6·21 |
| Phosphoric acid | 25·53 | 11·15 | 44·50 | 13·84 | 11·21 |
| Silica, &c. | 0·87 | 1·01 | 1·78 | 0·57 | 11·26 |
| Total amount | 101·09 | 99·58 | 100·27 | 102·42 | 97·80 |

In the ash only of the dandelion root is the silica sufficiently large in quantity to make a good distinction from coffee. Lupins and maize are distinguished from coffee by their low proportion of carbonic acid. The white lupin, both of the Levant and England, we find to contain a notable quantity of manganese. The oxide of iron is everywhere too low to be serviceable. Chlorine appears as low in maize as in coffee, but the proportion of that element is doubled in lupins, acorns, parsnips,—and nearly quadrupled in dandelion: a high proportion of phosphoric acid distinguishes maize, and we may add all the other cereals, from coffee.

The ash of the turnip root contains, according to Way and Ogston, from 9·54 to 14·82 per cent. of carbonic acid, which is very different from chicory, and nearly as high as in coffee. The sesquioxide of iron of turnip is also given even lower than in coffee,—from 0·14 to 0·66 per cent. Chlorine appears to be as abundant in the turnip, in the form of chloride of sodium, as in the chicory root.

According to the same excellent authorities, in beet-root-ash the carbonic acid varies from 15·23 to 21·61 per cent., and is therefore quite as high as in coffee-ash; the sesquioxide of iron, from 0·52 to 3·74 per cent., small as in coffee; the chlorine very large and distinctive, being represented by from 14·18 to 49·51 per cent. of chloride of sodium.

In the ash of the carrot, the carbonic acid is from 15·15 to 19·11 per cent.; the sesquioxide of iron, from 0·59 to 1·66 per cent.; chlorine nearly as in chicory, being represented by from 4·91 to 7·65 per cent. of chloride of sodium (Way and Ogston).

7. The action of the more ordinary chemical reagents upon infusions of coffee and chicory may now be noted. The indications thus obtained with coffee are unfortunately rendered much less characteristic by the torrefaction of the seed.

TABLE X.

Action of certain chemical reagents upon infusions of coffee and chicory.

| | Raw Coffee. | Roasted Coffee. | Raw Chicory. | Roasted Chicory. |
|---------------------|---|--|--------------------------------------|---|
| Potassa . . . | A bright red-dish-yellow liquid, and no precipitate. | Brownish-yellow liquid, and no precipitate. | Not altered. | Not altered. |
| Lime-water . . | Pale-yellow liquid ; on standing, becoming green at the surface ; no precipitate. | Reddish-brown, with shade of purple, and no precipitate. | Not altered. | Not altered. |
| Acetate of copper | Dirty-green precipitate. | Brownish-green precipitate. | Pale-green precipitate. | Gelatinous precipitate of a reddish-brown colour. |
| Perchloride of iron | Deep greenish-black precipitate. | Very dark greenish-black precipitate. | Blackish-brown-coloured liquid. | No effect. |
| Nitric acid . . | Bright red-coloured liquid. | Clear port-wine-coloured liquid. | No effect. | No effect at first ; on standing, port-wine colour. |
| Sulphuric acid . | Dirty blackish-brown-coloured liquid. | Dark blackish-brown-coloured liquid. | Deep blackish-brown-coloured liquid. | Brownish-black liquid. |
| Hydrochloric acid | Pale brownish-yellow liquid. | Port-wine-coloured liquid. | No effect. | Slightly darkens the liquid. |

In allowing a solution of unroasted coffee to stand, its green colour becomes gradually deeper. This change is due to oxidation and the formation of the viridic acid of Rochleder. It is greatly promoted by the presence of an alkali: an excess of lime brings out this colour very strongly in a day or two,—giving at first, however, a bright yellow colour. Subacetate of lead gives, in unroasted coffee, a yellow precipitate, which does not become green. An excess of acetate of copper gives a green precipitate

in abundance, which is brightened by the addition of an alkali. This copper precipitate has been used as a green pigment. The reactions above described are, however, much altered and obscured by the roasting of the coffee, and are therefore of little service for our present purpose.

It has already been stated that iodine produces no blue coloration in the infusion of either coffee or chicory. If the reagents named act clearly in a different manner upon any infusion from what they do upon pure coffee, a presumption of adulteration is obtained, but the indications must be of a positive and specific nature fully to establish adulteration.

8. Coffee was submitted to the usual process of distillation with soda-lime for the determination of its nitrogen. The proportion of nitrogen per cent. was, in coffee, Sample 1 (Table VII.), roasted, 2.93; in Sample 2, roasted, 2.62; in Sample 3, raw, 2.53, roasted, 2.70; in Sample 4, raw, 2.71; in Sample 5, raw, 2.50, roasted, 2.49. The proportion of nitrogen in roasted coffee appears therefore to lie between $2\frac{1}{2}$ and 3 per cent.

The nitrogen in a specimen of foreign chicory amounted, in the raw chicory, to 1.51 per cent.; in the same roasted, 1.42 per cent. The same of English growth gave, in the raw state, 1.86 per cent. of nitrogen; and in the roasted state, 1.74 per cent.

The proportion of nitrogen in coffee is therefore greater than in chicory; but the difference is not sufficiently marked to distinguish the two substances easily from each other. The conclusion may, however, be drawn, that less than 2 per cent. of nitrogen in coffee is a strong presumption of adulteration.

We may now advert to the peculiar and characteristic substances found in coffee, and the aid to be derived from them in the discovery of adulteration.

9. Professor Rochleder, who has devoted great attention to the analysis of coffee, gives the following enumeration of the substances found in the raw coffee-bean, with the formulæ of their elementary composition:—

| | C. | H. | O. | N. |
|-----------------------------|----|----|----|----|
| Woody fibre | 12 | 10 | 10 | |
| Cane sugar | 12 | 11 | 11 | |
| Fat { Palmitic acid | 32 | 32 | 4 | |
| { Oleic acid | 36 | 34 | 4 | |
| { Glycerine | 6 | 8 | 6 | |
| Legumin | 48 | 36 | 14 | 6 |
| Caffeic acid | 16 | 7 | 6 | |
| Caffeine | 16 | 10 | 4 | 4 |

To these Rochleder had lately added citric acid ($C_{12}H_5O_{11} + 3HO$), in the small proportion of 2 grains in a pound of coffee; also a trace, too small to be estimated by weight, of viridic acid ($C_{14}H_6O_7$). This last substance is the acid obtained by exposing solutions of the neutral and basic caffeates to the influence of the air. The green colour of raw coffee is believed by Rochleder to be owing to a small quantity of viridate of lime.

The evidence upon which Rochleder rests the existence of palmitic and citric acids in coffee does not appear to us quite decisive. The formulæ given by that chemist for both caffeic and viridic acids are doubtful.

It is also stated by Rochleder, that when dried caffeic acid is submitted to destructive distillation, a small quantity of crystals were obtained, which he considered to be pyrocatechine. The experiment repeated by us on a considerable scale gave a negative result.

Rochleder finds caffeic acid in Paraguay tea (*Ilex Paraguayensis*), as well as in coffee. This statement we must also doubt. The acid of the Paraguay tea has been examined by us, and found to have a certain resemblance to caffeic acid, but not to be identical with it. Free caffeic acid, when strongly heated in an open vessel, emits the peculiar odour of roasted coffee; but the acid from Paraguay tea emits a perfectly different odour when similarly treated.

The sugar of coffee may be inferred to exist in a peculiar condition, as was before hinted, from the fact that when the coffee is roasted, none of its sugar appears to be converted into grape-sugar, as it does not affect Trommer's test; while, when 7 grains of cane-sugar were added to 100 grains of coffee, and the whole roasted in the usual way, abundant indications of grape-sugar were obtained by the same test.

M. Payen gives the proportional quantities of the different substances which he finds in raw coffee as follows:—

| | |
|---|---------------|
| Cellular tissue | 34·000 |
| Hygroscopic water | 12·000 |
| Fats | 10· to 13·000 |
| Starch, sugar, dextrin, and vegetable acids | 15·500 |
| Legumin | 1·000 |
| Chlorogenate of potash and caffeine . . . | 3·500 |
| Nitrogenous portion | 3·000 |
| Free caffeine | 0·800 |
| Thick insoluble ethereal oil | 0·001 |
| Aromatic oil | 0·002 |
| Mineral constituents: potash, lime, magnesia, phosphorus, sulphur, silica, and traces of chlorine | 6·697 |

Payen's chlorogenic acid is the same as the caffeic acid of Rochleder and Pfaff. Payen believed that he had obtained from coffee a crystalline double salt of this acid, containing potash and caffeine; but this observation has not been confirmed.

The proportion of fat in the coffee bean is remarkably high, being generally stated at 10 or above 10 per cent. We found at least 8·9 per cent. of fat readily extracted by ether. In chicory the proportion of natural fat is scarcely appreciable; but it is brought up by the fat added in the process of roasting the chicory.

10. Some uncertainty existing respecting the proportion of the active principle, caffeine, in coffee, the point was particularly inquired into. The following process was adopted:—The raw coffee was ground fine, having been previously well dried at 212° to facilitate that operation. A decoction was then made of 1000 grains, by the repeated application of boiling water, so as to exhaust the coffee of all soluble matter. The solution was concentrated a little by evaporation. The acid of the coffee, and certain other substances, were now entirely precipitated by the addition, first, of the neutral acetate of lead, and then of the subacetate of lead. These insoluble matters were removed from the liquid by filtration. The excess of lead in solution was then thrown down by means of hydrosulphuric acid.

The liquid, after this preparation, was evaporated to dryness, and the dry matter left was exhausted by means of strong spirit of wine (sp. gr. 0·840). The alcoholic solution was concentrated by evaporation, and allowed to stand in a nearly syrupy state for about ten days, in order to crystallise. The crystals, which are caffeine, were collected upon a small filter, and compressed powerfully to remove the mother liquor. These crystals were redissolved in a small quantity of water, the solution evaporated, and crystallised anew. It gave almost nothing but caffeine, in long silky white needles, with little or no colour. The proportion of caffeine obtained in five experiments, made upon different samples of coffee, was as follows:—

CAFFEINE IN RAW COFFEE.

| | | | | | |
|---------------------|---|---|---|------|-----------|
| In Native Ceylon | . | . | . | 0·80 | per cent. |
| „ „ „ | . | . | . | 0·80 | „ „ |
| „ „ „ | . | . | . | 1·01 | „ „ |
| „ Plantation Ceylon | . | . | . | 0·54 | „ „ |
| „ „ „ | . | . | . | 0·83 | „ „ |

The caffeine of the wild coffee appears to exceed that of the cultivated plant; the mean proportion of caffeine in Native Ceylon being 0·87 per cent., and in Plantation Ceylon 0·69 per cent.

The mean average of the whole five samples is 0·80 per cent. of caffeine. Probably the actual quantity of caffeine in the coffee bean is from 0·75 to 1 per cent., allowance being made for losses in the separation.

The proportion of theine (or caffeine) in tea is considerably greater, and more easily extracted. Two pounds of fine strong Congou yielded 2·93 grains of theine, or 2·09 per cent.

When it is merely desired to extract caffeine from raw or roasted coffee, without reference to quantity, the general process for the extraction of organic bases by means of ether suffices. Lime is added to the infusion of coffee, which is then evaporated to dryness upon a water-bath. The extract may be divided by means of clean sand, and then agitated with ether. The caffeine crystallises as the ether evaporates, or it may be re-dissolved in water, and crystallised again. We believe that the caffeine from 10 per cent. of coffee in a mixture might be extracted in sufficient quantity for its identification by the preceding simple process. Caffeine, when once obtained, is fully recognised by its easy sublimation, and also by its action with nitric acid, in which it resembles uric acid. When the solution of caffeine in nitric acid is evaporated to dryness, and exposed to ammoniacal gas, it is covered by a pink blush, like murexide.

The only other substances besides coffee in which caffeine is known to exist, are tea, Paraguay tea, and a species of chocolate made from the *Gaurana officinalis* or *Paullinia sorbilis*.

11. Chemists generally are disposed to refer the flavour and peculiar properties of coffee, as a beverage, more to its acid—the *caffeic acid* (particularly after that substance is modified in its properties by roasting), than to any other constituent of the seed. Rochleder considers this acid as belonging to the tannin class of substances, and calls it tanno-caffeic acid. But as caffeic acid does not precipitate gelatine, it is deficient in the most characteristic quality of the tannic acids. Caffeic acid, in the present state of our knowledge, appears to be confined to the coffee plant.

We have observed a property of caffeic acid which facilitates the detection of that substance, and consequently of coffee, in a mixture. Caffeic acid appears to be analogous to kinic acid, the acid of cinchona barks, for it yields kinone when oxidated by means of sulphuric acid and binoxide of manganese. To observe this property, the coffee is boiled with water and a little slaked lime, the infusion filtered, and evaporated down to the consistence of a syrup. The syrupy liquid is then mixed in a retort with four times its weight of binoxide of manganese, and 1 part of oil of vitriol diluted with an equal bulk of water. Sufficient heat is

produced by the action of sulphuric acid upon the other materials, to bring over the greater portion of the kinone, and the lamp need not be applied till towards the close of the operation. The distillate consists of yellow crystals of kinone, which usually coat the neck and sides of the retort, and a bright yellow liquid, which is a saturated aqueous solution of kinone, with a considerable quantity of formic acid. Kinone is easily discernible by its volatility and peculiarly acrid odour, which greatly resembles that of chlorine. The solution of kinone gives with ammonia a sepia-black colour, and becomes reddish-brown with hydrosulphuric acid. It is decolorised by sulphurous acid. The beautiful green hydrokinone is obtained by exactly neutralising the solution of the yellow kinone with sulphurous acid, great care being taken not to introduce the latter in excess.

The peculiar acid of Paraguay tea agrees with caffeic acid (to which it is no doubt related) in yielding kinone to similar oxidising agencies: so does the acid of the leaves of common holly (*Ilex aquifolium*), tea, and the whole of the *cinchona* tribe.

The *prune* tribe of plants, including the sloe, cherry, laurel, &c., the seeds of which yield prussic acid, all contain amygdalin, or some similar principle. Now all of these, when oxidised in the same manner as the former class, yield oil of bitter almonds, and so can be recognised.

The *willow* and *poplar* tribe, on the other hand, yield oil of *Spirea ulmaria* (salicylous acid), a very characteristic substance.

The tests for kinone can be applied in a few minutes, and they are sufficient to indicate the presence of 10 or 12 per cent. of coffee in a mixture.

12. The root of *chicory* presents no feature of a marked nature, beyond its large proportion of sugar and the composition of its ash, which have both been sufficiently adverted to. The proportion of fat naturally in the root is quite insignificant. In an infusion of the fresh undried root, neutral acetate of lead appears to throw down the whole acids of chicory, and the subacetate of lead produces no further precipitate in the liquid. But the root appears to undergo a considerable modification by being dried at a temperature not exceeding 212°. Its infusion now gives a second precipitate with subacetate of lead following the neutral acetate. Both of these precipitates can be well enough washed; but when the attempt was made to decompose either of them by means of hydrosulphuric acid, a mucilaginous liquid was obtained, from which the sulphide of lead does not fall, unless with a considerable addition of alcohol. The acid precipitates appear most indeterminate, and afford nothing crystalline. A great deal of pectin-looking substance is present. Chicory also appears to

possess about one-fourth of the quantity of inulin that is contained in the dahlia root, and starch in no other form, the infusion of chicory giving only a brown with iodine, and no blue. Chicory appears to contain no oxalic, malic, citric, or any other crystallisable organic acid. The other sweet roots, beet, turnip, &c., also, like chicory, present little that is tangible in their chemical properties. But the high colour of the infusions of all these roots when roasted, the great density of their solutions, and their fermentability, afford sufficient means for distinguishing them from coffee, and for discovering their admixture with that substance.

The properties of a great variety of other vegetable substances, which might possibly be employed in the adulteration of coffee, are exhibited in the early tables of this Report.

On Circumstances modifying the Action of Chemical Affinity.*

By J. H. Gladstone, Ph.D., F.R.S.

IT is among the facts in chemical science which admit of no dispute, that a substance frequently shows a greater tendency to combine with one body than with another. This has usually received the appellation "elective attraction," or "elective affinity." It is also perhaps universally allowed that the manifestations of this elective affinity are greatly influenced by the insolubility or the volatility of the original substances, or of the resulting compounds. The degree of temperature, the respective masses of the different substances, the presence of other bodies, and many circumstances beside these, are supposed to modify the result.

The attempt has frequently been made to construct tables showing the relative strength of affinity of different substances for some particular body, and Guyton de Morveau even endeavoured to give a numerical expression to them. In treating of this subject, the elaborate disquisition of Bergman, "*De Attractionibus Electivis*," must be referred to; in which he illustrates at once the chemical fact, and the meaning of the term, by supposing *A* to be a substance united to *c*, and that, on the addition of *b*, the *c* is excluded, and the union of the latter substance with *A* is brought about; in which case, he says, *b* has a stronger elective attraction for *A* than *c* has. He, in common with most chemists, both of his own and of later times, takes it for granted that if *b* decomposes *Ac*, it does so completely. The Swedish chemist

* Phil. Trans. 1855, p. 179.

gives the results of nearly 2000 reactions in one table, the first column of which exhibits the following substances arranged according to their affinity for sulphuric acid, commencing with what he conceived the most powerful:—baryta, potash, soda, lime, magnesia, ammonia, zinc, manganese, iron, lead, tin, cobalt, copper, nickel, bismuth, arsenic, mercury, antimony, silver, gold, platinum, alumina, sesquioxide of iron, water, phlogiston. The suitability of some of the methods employed for arriving at these results, has never, as far as I know, been questioned; for instance, that zinc has a stronger affinity for sulphuric acid than manganese, or iron, or lead has, because it will separate any one of these metals from its solution in the said acid. Other methods, however, are more open to objection,—such, for example, as that which led Bergman to place baryta at the head of the series, because it took sulphuric acid from every other base. To such deductions as this, drawn from precipitation, it may be objected that the tendency of the two bodies to combine has arisen more or less from the insolubility of the compound. Berthollet adopted this view, and in his “*Recherches sur les Lois de l’Affinité*” he endeavoured to prove “*que les affinités électives n’agissent pas comme des forces absolues par lesquelles une substance seroit déplacée par une autre dans une combinaison; mais que, dans toutes les compositions et les décompositions qui sont dues à l’affinité élective, il se fait un partage de l’objet de la combinaison entre les substances dont l’action est opposée, et que les proportions de ce partage sont déterminées, non seulement par l’énergie de l’affinité de ces substances, mais aussi par la quantité avec laquelle elles agissent, de sorte que la quantité peut suppléer à la force de l’affinité pour produire un même degré de saturation.*”

These two conflicting views were much discussed at the time when they were propounded; the attention subsequently paid to the laws of stoichiometry has removed much of the difficulty in which the subject was then involved; Gay-Lussac has pointed out the erroneous idea of cohesion that obscured the reasoning of Berthollet; and yet the amount of truth contained in either of these opposite opinions remains still an open question.

It is now some years since I first began to reason, and occasionally to experiment, upon this subject. Since that time, Malaguti has published a paper bearing upon it, which will be referred to subsequently; Bunsen and Debus have experimented, and independently arrived at a very remarkable law; and Williamson has on more than one occasion vindicated the views of Berthollet.

Bunsen* exploded together carbonic oxide, hydrogen, or

* Ann. Ch. Pharm. lxxxv. 137.

cyanogen with oxygen, and, after varying his experiments greatly, deduced conclusions tending to show a simple atomic relation between the products of the combustion, and a sudden transition from one ratio to another, as the proportions of the original gases were varied. Debus* examined the phenomena presented in the precipitation of a mixture of the hydrates of lime and baryta by carbonic acid, and of the hydrochlorates of these earths by carbonate of soda, and arrived at analogous results.

In each of these cases, however, the first products of the chemical combination were removed at once from the field of action. It is evidently quite another case when the products themselves remain free to react. A mixture of two salts in solution, which do not produce a precipitate, affords a case where this requisite is fulfilled. Let AB and CD be such salts. According to the one view, when mixed, they will either remain without mutual action, or, should the affinities so preponderate, they will become simply AD and CB, the excess of either original salt remaining inactive. According to the other view, A will divide itself in certain proportions between B and D, while C will do the same in the inverse ratio, the said proportions being determined not solely by the differences of energy in the affinities, but also by the differences of the quantities of the bodies. Again, supposing the latter view to be correct, another question will arise, — Does the amount of AD or CB produced increase in a gradual manner with the relative increase of AB; or do sudden transitions take place under these circumstances, such as Bunsen and Debus observed in their experiments?

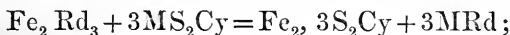
It was to the elucidation of these questions that I applied myself. In the majority of instances, it is impossible to ascertain what has taken place when a mixture of the kind alluded to has been made; but the physical properties of salts will sometimes give an indication. Colour seemed to offer the best means of solving the problem; yet even here a difficulty arose from the fact that many bases, such as nickel, give the same-coloured solution when combined with different acids, and *vice versâ*. Sesquioxide of iron, however, appeared to promise good results, since many of its salts are intensely coloured, while others are almost colourless.

FERRIC SULPHOCYANIDE.

If a soluble sulphocyanide be mixed with a ferric salt, a red solution results, indicating the formation of the ferric sulphocyanide. Suppose three equivalents of the sulphocyanide be

* Ann. Ch. Pharm. lxxxv. 103; lxxxvi. 156; lxxxvii. 238.

mixed with one equivalent of the metallic salt, we have the exact proportions theoretically necessary for the production of $\text{Fe}_2, 3\text{S}_2 \text{Cy}$. The first question to be solved is,—In such a case does the whole of the iron and of the sulphocyanogen combine as ferric sulphocyanide, or does it not? If Bergman's view be correct, the decomposition will be in accordance with the following simple formula (Rd standing for any salt radical, and M for any metal)—



and it will not matter what metal is represented by M, or what salt radical by Rd, provided only that a double decomposition *does* take place. Besides which, the addition of a larger quantity of either one of the original compounds will not increase the colour; for there is but one sesquisulphocyanide of iron, and the whole of the iron, or of the sulphocyanogen (as the case may be), has been already saturated. If, however, Berthollet's view be correct, the decomposition will not be so complete as to form merely $\text{Fe}_2, 3\text{S}_2 \text{Cy}$ and 3M Rd , but in addition to these two salts there will be certain portions of the two original salts still remaining as such in the solution. This will become manifest by an amount of colour being obtained which is not equal to what would have been produced had the whole of the iron entered into combination with the sulphocyanogen: and the requirements of the theory will lead us moreover to expect that the amount of ferric sulphocyanide (and consequently the depth of colour) will depend in a great measure on the nature of M or Rd, and will be increased by each addition of either the soluble sulphocyanide or the ferric salt.

The following were the preliminaries for the complete determination of this question:—

Aqueous solutions of the ferric chloride, nitrate, sulphate, acetate, and citrate, were prepared of known strength; as, also, of sulphocyanide of potassium, barium, and mercury; of hydro-sulphocyanic acid, and of various potash salts.

In order to compare the depth of colour produced on the admixture of these solutions, it was necessary to have vessels of colourless glass of a uniform character. Ordinary precipitating glasses, holding about five ounces, were found peculiarly fitted for the purpose: being blown, and not moulded, they are very translucent; they are easily obtained devoid of colour; and, although not strictly uniform in size, it was easy to pick out a sufficient number which would furnish every requisite for the experiment. This was tested by dividing a coloured solution into two equal parts, and pouring one-half into one glass, and the other half into another: if the two solutions appeared then of a perfect equality of tint, nothing more could be desired. When two or more coloured solutions were to be compared, the best method was

found to be to place the glasses containing them on a stand before the window, across the pane of which was stretched a piece of tissue-paper about three inches in depth. The experiments were almost always performed when the sun was shining, but not on the window itself, as that was found to be disadvantageous. By observing the coloured solutions against the evenly illuminated tissue-paper, most exact results could be obtained, especially after a little practice. If the object was to observe the amount of dilution necessary to reduce one coloured solution to the same tint as another, distilled water was added, and thoroughly mixed with it, until equal bulks of the two solutions appeared alike. The amount of water added was of course easily measured in a graduated vessel. My own observation was always checked by that of my assistant; and if we differed, I generally adopted his view, since, having no idea of what result was to be expected, his judgment was the more impartial. I may also state in this place, that it was found unnecessary to let a freshly mixed solution containing a sulphocyanide stand any length of time, for it assumed instantaneously its proper amount of colour: two mixtures, similarly prepared, were always found to be of precisely the same shade; and everything conspired to give me great and increasing confidence in the validity of testimony drawn from the colour of a solution.

The first object to be determined evidently was, whether, on mixing three equivalents of sulphocyanide of potassium with one equivalent of the ferric salt, say the chloride, the full depth of colour possible from the combination of all the sulphocyanogen with all the iron was actually obtained. That this was not the case was seen at once, for on adding to such a mixture either more sulphocyanide of potassium, or more chloride of iron, the colour was increased. This showed also the influence of mass, which will be exhibited quantitatively in due course; but before doing so it is necessary to advert to another part of the inquiry, viz.—

The dependence of the amount of the coloured salt on the nature of the other substances present in the solution, but which are not immediately concerned in its formation.—In order to investigate this point, solutions of each of the ferric salts, containing exactly the same amount of iron, were mixed with the sulphocyanide of potassium solution, in the proportion of one equiv. of the former to three of the latter. The five mixtures were equally diluted. At a glance it was evident that a widely different amount of red sulphocyanide of iron had been formed. The solution containing the ferric citrate was still green; that containing the acetate was red, but by no means deep in colour, and of a yellowish tint; while those containing the sulphate, nitrate, or chloride, were of an intense red. The following are the relative amounts of dilu-

tion required to bring these four last-mentioned solutions to the same tint:—

3 equivalents sulphocyan. potassium + 1 equivalent ferric nitrate diluted to 100 parts.

3 equivalents sulphocyan. potassium + 1 equivalent ferric chloride diluted to 89·4 parts.

3 equivalents sulphocyan. potassium + 1 equivalent ferric sulphate diluted to 65·2 parts.

3 equivalents sulphocyan. potassium + 1 equivalent ferric acetate diluted to 20 parts.

The numbers 100, 89·4, 65·2, and 20 therefore represent the relative amounts of the ferric sulphocyanide contained in these several mixtures.*

In reference to the mixture of ferric citrate with sulphocyanide of potassium, the question presents itself,—Does absolutely no interchange take place between them, or does a partial though very minute formation of ferric sulphocyanide occur, in accordance both with the law of Berthollet and the analogy of the other cases? The latter conclusion will appear probable from the following observations. Although the yellowish-green tint of the citrate still remains after the addition of three equivalents of the sulphocyanide, six equivalents almost remove it, and a larger quantity renders the solution colourless. No red colour ever appears in a very dilute solution, but this destruction of the green appears to point to the presence of a sufficient amount of the complementary colour to neutralise it; and if sulphocyanide of potas-

* After this paper had been read, the following note was appended:—That two or more solutions of the same salt in the same solvent, and of equal depth of colour, are of the same strength, requires no proof. Hence I apprehend no objection can be raised against the conclusion that the gross amounts of salt dissolved in the different solutions are directly proportional to their volume. But it may be objected, that though this is true of the solutions when diluted to an equality of colour, it is not necessarily true of the solutions before they were diluted, for the solvent may exercise some chemical action on the coloured salt, absolutely increasing or diminishing its quantity. Should such be the case, it appears to me actually the most correct plan of proceeding to reckon the result when the solutions of the coloured salt are of equal strength,—that is to say, when the solvent is in each case in the same proportion to the dissolved salt; for the disturbing influence of the solvent is thus practically got rid of, by its reduction to an equality in all the solutions compared.

There is, however, a more serious objection,—namely, that the solvent may act differently on the coloured salt, according to the nature or the quantity of the colourless salts present at the same time in the several solutions; or that these salts may act differently according to the amount of solvent with which they are conjoined. That this may be the case to a slight extent is very possible, but the experiment recorded on page 79 shows that it was too inconsiderable to be appreciated in the cases there submitted to examination. As this is an important matter, I have repeated the experiment in a great variety of ways, and have satisfied my mind that the amount of error arising from this cause must be quite insignificant—at any rate as far as the ferric sulphocyanide is concerned. The slight differences that do occur are rather in the character than in the intensity of the colour.

sium be added in large excess to a strong solution of citrate of iron, an unmistakeable red ensues.

Similar experiments were tried in which the same ferric salt was employed, but different sulphocyanides. Two portions of nitrate of iron, each representing one equivalent, were mixed, the one with six equivalents of sulphocyanide of barium, the other with a corresponding amount of the potassium salt. A deep red resulted in both instances, but 1000 gr. meas. of the solution containing the potassium compound required the dilution of that containing the barium salt to only 880 gr. meas. to bring it to an equality of colour. The solution of sulphocyanide of mercury produced a scarcely perceptible reddening when added to the ferric nitrate.

These experiments suffice to show, that on mixing together solutions of soluble sulphocyanides and of ferric salts, the amount of sesquisulphocyanide of iron formed depends in a great measure on the nature of the substances previously combined with the sulphocyanogen and with the metallic oxide. The question naturally arises,—Does the converse of this hold good? If a solution of sesquisulphocyanide of iron be mixed with some other salt, not capable of forming a precipitate with it, will that also cause the distribution of the elements into *four* salts, manifesting itself by a diminution of the colour? and if so, will that vary according to the nature of the other salt?

| | I. | II. | III. | IV. |
|--|--------------|-------|-------|-------|
| Volume of original solution + salt added . | 70 m. | 64 m. | 34 m. | 60 m. |
| Mixture containing the nitrate . . . | 80 | 77 | 41 | 62 |
| Mixture containing the chloride . . . | 90 | 90 | 56 | 68 |
| Mixture containing the sulphate . . . | 150 | 160 | 124 | 85 |
| Mixture containing the acetate . . . | 270 | 220 | 164 | 120 |
| Mixture containing the citrate . . . | trace of red | green | | |

Six equal portions of as pure sesquisulphocyanide of iron as could be prepared were taken: one was kept as a standard; to the other five were added respectively equal portions of the nitrate, hydrochlorate, sulphate, acetate, and citrate of potash. In each case, the colour was reduced. Column I. in the annexed table shows the amount to which the standard had to be diluted before it was brought down to an equality in colour with the different mixtures. Column II. represents a similar experiment, in which a red mixture of one equivalent of sesquichloride of iron and twelve equivalents of sulphocyanide of potassium was employed

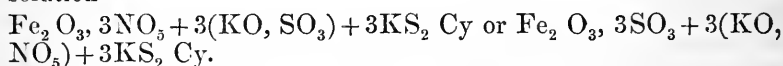
instead of the actual ferric sulphocyanide. In III. a mixture of ferric sulphate and sulphocyanide of potassium was employed; in IV. the same, with a large excess of sulphuric acid.

These experiments might be varied *ad infinitum*, all proving the influence on the resulting colour of the *nature* of a substance mixed with the ferric sulphocyanide. Other organic acids, such as the oxalic and the tartaric, were found to reduce the red very rapidly.* As might be expected, also, the diversity of effect is not confined to differences in the *acid* present. The addition of a protosalt of iron has a very great effect in reducing the colour of the ferric sulphocyanide: baryta and lime salts act powerfully. A solution of chloride of mercury (as was observed long ago) very speedily removes the colour.

The colour of a mixture not dependent on the manner in which the constituents were originally arranged.—On more closely examining the above results, it will be seen that whether ferric citrate be mixed with sulphocyanide of potassium, or ferric sulphocyanide with citrate of potash, the resulting liquids contain but the merest trace of the red salt; it appears also that the deepest colour is obtained on mixing either ferric nitrate with sulphocyanide of potassium, or ferric sulphocyanide with nitrate of potash; whilst the mixtures containing compounds of acetic, sulphuric, and hydrochloric acids are intermediate in colour in regular order. Mercury also seems to exert the most powerful affinity for sulphocyanogen in whatever way they are brought together. This suggests the conclusion that the amount of sulphocyanide of iron in a mixture of salts does not depend on the *manner* in which the different substances were at first combined. The experiment above described was incapable of affording a quantitative demonstration of this, as a perfectly pure and definite sulphocyanide of iron was not obtained; but the following arrangement was made to put it to a rigid test. Two mixtures were made of the solutions of known strength, so that each contained one equivalent of ferric oxide, three equivalents of potash, three equivalents of nitric acid, and three equivalents of sulphuric acid. To each was added 1.5 equiv. of sulphocyanide of potassium. The colours resulting in the two cases were so nearly identical, that the first diluted to 1770 gr. meas. just equalled the second diluted to 1820 gr. meas. Another 1.5 equiv. of sulphocyanide of potassium was added to each. The two solutions appeared now identical in colour; they certainly did not differ by 1 degree in 80. The amount of sulphocyanide of potassium in each was then doubled: the resulting colours could not be distinguished from each other. It appears, there-

* Pelouze has observed the different effects of different acids, *Ann. Chim. et Phys.* xliv. 216.

fore, that it makes no difference whether there be mixed in solution



The influence of the mass of one of the substances that produce the coloured salt.—The influence of mass has yet to be considered quantitatively. For this purpose, two mixtures were prepared, each containing one equiv. of the ferric nitrate, and three equivs. of the sulphocyanide of potassium solution. They were both diluted so as to occupy the same volume. The one was kept as a standard of comparison; with the other, additional portions of sulphocyanide of potassium were mixed; and as that increased the colour, it was diluted till brought to an equality with the standard solution.

| Ferric nitrate. | Sulphocyan. of potassium. | Red salt produced. | Ferric nitrate. | Sulphocyan. of potassium. | Red salt produced. |
|-------------------------|---------------------------|--------------------|------------------------|---------------------------|--------------------|
| 1 equiv. + 3 equivs. | | 88 | 1 equiv. + 63 equivs. | | 356 |
| 1 equiv. + 6 equivs. | | 127 | 1 equiv. + 99 equivs. | | 419 |
| 1 equiv. + 9.6 equivs. | | 156 | 1 equiv. + 135 equivs. | | 457 |
| 1 equiv. + 12.6 equivs. | | 176 | 1 equiv. + 189 equivs. | | 508 |
| 1 equiv. + 16.2 equivs. | | 195 | 1 equiv. + 243 equivs. | | 539 |
| 1 equiv. + 19.2 equivs. | | 213 | 1 equiv. + 297 equivs. | | 560 |
| 1 equiv. + 28.2 equivs. | | 266 | 1 equiv. + 375 equivs. | | 587 |
| 1 equiv. + 46.2 equivs. | | 318 | | | |

On comparing these numbers, it will be at once evident that each addition of the sulphocyanide produced relatively a smaller increase of colour. In the full paper, these results, and those of a similar character which follow, are represented by curves, of which the ordinates express the proportionate amount of red salt, and the abscissæ the number of equivalents of the sulphocyanide added.

The influence of mass was again tried by means of additional portions of ferric nitrate instead of additional sulphocyanide of potassium. The following are the results of the observations reduced as before:—

| Sulphocyan. of potassium. | Ferric nitrate. | Red salt produced. | Sulphocyan. of potassium. | Ferric nitrate. | Red salt produced. |
|---------------------------|-----------------|--------------------|---------------------------|-----------------|--------------------|
| 3 equivs. + 1 equiv. | | 88 | 3 equivs. + 5 equivs. | | 138 |
| 3 equivs. + 2 equivs. | | 110.5 | 3 equivs. + 6 equivs. | | 144 |
| 3 equivs. + 3 equivs. | | 122 | 3 equivs. + 10 equivs. | | 161 |
| 3 equivs. + 4 equivs. | | 131 | 3 equivs. + 14 equivs. | | 174 |

It is not difficult to bring this experiment into uniformity with the preceding so as to form in fact a continuation of it, one equiv. of ferric nitrate being combined with less than three equivs. of sulphocyanide of potassium. For, expressing the number of equivalents of the iron salt by x , and the comparative amount of ferric sulphocyanide by y , the general formula of the terms in the above table will be, K denoting the potassium and F the iron salt, —

$$3K + xF = y,$$

which may evidently be reduced to a unity of F by dividing by x , thus —

$$F + \frac{3}{x}K = \frac{y}{x}.$$

On this principle the experiment may be thus tabulated: —

| Ferric nitrate. | Sulphocyan. of potassium. | Red salt produced. | Ferric nitrate. | Sulphocyan. of potassium. | Red salt produced. |
|------------------------|---------------------------|--------------------|------------------------|---------------------------|--------------------|
| 1 equiv. + 3 equivs. | | 88 | 1 equiv. + 0.6 equiv. | | 27.6 |
| 1 equiv. + 1.5 equiv. | | 55.25 | 1 equiv. + 0.5 equiv. | | 24 |
| 1 equiv. + 1 equiv. | | 40.66 | 1 equiv. + 0.3 equiv. | | 16.1 |
| 1 equiv. + 0.75 equiv. | | 32.75 | 1 equiv. + 0.21 equiv. | | 12.43 |

It need scarcely be explained, that had the whole of the sulphocyanogen present in the above experiment united itself with the iron, the second term would have indicated 44 degrees instead of 55.25, the third 29.33, and so on.

In order to confirm, by a more direct experiment, the result just arrived at, two mixtures were made, consisting of 1 equiv. of ferric nitrate, and 0.24 equiv. of sulphocyanide of potassium. The experiment was conducted as in the previous cases.

| Ferric nitrate. | Sulphocyan. of potassium. | Red salt produced. | Ferric nitrate. | Sulphocyan. of potassium. | Red salt produced. |
|-------------------------|---------------------------|--------------------|--------------------------|---------------------------|--------------------|
| 1 equiv. + 0.24 equiv. | | 19 | 1 equiv. + 3.57 equivs. | | 97.8 |
| 1 equiv. + 0.48 equiv. | | 29.7 | 1 equiv. + 4.44 equivs. | | 108.2 |
| 1 equiv. + 0.78 equiv. | | 39.4 | 1 equiv. + 5.58 equivs. | | 119 |
| 1 equiv. + 1.05 equiv. | | 48.7 | 1 equiv. + 7.08 equivs. | | 134.3 |
| 1 equiv. + 1.31 equiv. | | 60.2 | 1 equiv. + 8.64 equivs. | | 147.3 |
| 1 equiv. + 1.83 equiv. | | 69 | 1 equiv. + 10.29 equivs. | | 158.1 |
| 1 equiv. + 2.22 equivs. | | 76.5 | 1 equiv. + 11.79 equivs. | | 167.8 |
| 1 equiv. + 2.88 equivs. | | 86.3 | | | |

The regularity of this increase of colour (as exhibited to the eye in the curves) is a proof that no law obtains under the circumstances of the experiment, similar to that observed and enunciated by Bunsen. There is nowhere any sudden increase in the amount of ferric sulphocyanide formed. If the partition of the bases and acids in the mixture really take place at first in atomic proportions, it is evident that, being at full liberty to act and react, the salts arrange themselves according to their respective mass, without reference to their respective atomic weights.

The effect of mass on the formation of ferric sulphocyanide in a mixture of salts, where other substances replaced the nitric acid or the potash, was also tried.

The two following tables represent similar experiments with the ferric sulphate and chloride.

| Ferric sulphate. | Sulphocyan. of potassium. | Red salt produced. | Ferric sulphate. | Sulphocyan. of potassium. | Red salt produced. |
|-----------------------|---------------------------|--------------------|------------------------|---------------------------|--------------------|
| 1 equiv. + 3 equivs. | | 88 | 1 equiv. + 45 equivs. | | 318 |
| 1 equiv. + 6 equivs. | | 128 | 1 equiv. + 57 equivs. | | 355 |
| 1 equiv. + 9 equivs. | | 153 | 1 equiv. + 69 equivs. | | 390 |
| 1 equiv. + 12 equivs. | | 177 | 1 equiv. + 81 equivs. | | 418 |
| 1 equiv. + 15 equivs. | | 198 | 1 equiv. + 93 equivs. | | 440 |
| 1 equiv. + 20 equivs. | | 223 | 1 equiv. + 105 equivs. | | 458 |
| 1 equiv. + 24 equivs. | | 241 | 1 equiv. + 123 equivs. | | 486 |
| 1 equiv. + 30 equivs. | | 263 | 1 equiv. + 147 equivs. | | 513 |
| 1 equiv. + 36 equivs. | | 288 | 1 equiv. + 195 equivs. | | 538 |

| Ferric chloride. | Sulphocyan. of potassium. | Red salt produced | Ferric chloride. | Sulphocyan. of potassium. | Red salt produced. |
|-------------------------|---------------------------|-------------------|--------------------------|---------------------------|--------------------|
| 1 equiv. + 3 equivs. | | 88 | 1 equiv. + 65.4 equivs. | | 338 |
| 1 equiv. + 9 equivs. | | 148 | 1 equiv. + 83.4 equivs. | | 370 |
| 1 equiv. + 15 equivs. | | 190 | 1 equiv. + 107.4 equivs. | | 400 |
| 1 equiv. + 21 equivs. | | 216 | 1 equiv. + 131.4 equivs. | | 428 |
| 1 equiv. + 28.8 equivs. | | 246 | 1 equiv. + 155.4 equivs. | | 456 |
| 1 equiv. + 41.4 equivs. | | 286 | 1 equiv. + 191.4 equivs. | | 488 |
| 1 equiv. + 53.4 equivs. | | 312 | 1 equiv. + 239.4 equivs. | | 528 |

A glance at these tables will show that, although the actual amount of ferric sulphocyanide produced from the same quantity of the sesquinitrate, chloride, or sulphate of iron, varies greatly,

yet the increase of colour on the addition of more sulphocyanide of potassium maintains a somewhat similar ratio in each case. The variations that do exist, arise, I am disposed to think, mainly from errors in the experiment; and this opinion is founded not only on the observations above detailed, but upon others of a shorter range, which it was not considered necessary to record, especially as the three given were the last of their respective kinds which I made, and on that account, I believe, worthy of the greater reliance. None of the others, I may remark, differed materially from them.

I have in vain endeavoured, by the aid of my friend, Mr. Henry Watts, to find an equation which will resolve the curves deduced from the above observations. They do not appear to belong to the second order.

For the purpose of seeing whether the same ratio was maintained where a much smaller proportion of red sulphocyanide was formed, the experiment was repeated with the ferric acetate.

| Ferric acetate. | Sulphocyan. of potassium. | Red salt produced. | Ferric acetate. | Sulphocyan. of potassium. | Red salt produced. |
|----------------------|---------------------------|--------------------|-----------------------|---------------------------|--------------------|
| 1 equiv. + 1 equiv. | | 62.4 | 1 equiv. + 11 equivs. | | 232 |
| 1 equiv. + 3 equivs. | | 88 | 1 equiv. + 13 equivs. | | 304 |
| 1 equiv. + 5 equivs. | | 108 | 1 equiv. + 15 equivs. | | 352 |
| 1 equiv. + 7 equivs. | | 133 | 1 equiv. + 19 equivs. | | 398 |
| 1 equiv. + 9 equivs. | | 187 | | | |

Here we have not only an entirely different ratio, but one of an irregular character. It is evident there is some interfering action; what that is will be seen when the ferric acetate itself is made the subject of experiment.

A similar experiment on the influence of mass was tried with hydrogen in the place of potassium.

| Ferric nitrate. | Hydrosulphocyanic acid. | Red salt produced. | Ferric nitrate. | Hydrosulphocyanic acid. | Red salt produced. |
|-----------------------|-------------------------|--------------------|-----------------------|-------------------------|--------------------|
| 1 equiv. + 2 equivs. | | 66 | 1 equiv. + 20 equivs. | | 288 |
| 1 equiv. + 4 equivs. | | 108 | 1 equiv. + 24 equivs. | | 315 |
| 1 equiv. + 6 equivs. | | 142 | 1 equiv. + 30 equivs. | | 353 |
| 1 equiv. + 8 equivs. | | 168 | 1 equiv. + 38 equivs. | | 400 |
| 1 equiv. + 12 equivs. | | 217 | 1 equiv. + 46 equivs. | | 440 |
| 1 equiv. + 16 equivs. | | 257 | | | |

The ratio here is regular, but more rapid than in the case of the potassium salt.

Method of determining the actual amount of the coloured salt in a given mixture.—From the experiments above recorded, it would seem probable that no amount of sulphocyanide of potassium added to a ferric salt will absolutely convert the whole of it into the sesquisulphocyanide of iron. Yet we can easily judge where this result will be very nearly attained. Thus 400 equivalents of the sulphocyanide, added to one of the ferric nitrate, must give a close approximation. A somewhat larger quantity will do the same with the sulphate. Indeed, it was found by experiment that 500 equivalents of the sulphocyanide added to each of the three principal ferric compounds, caused as nearly as possible the same intensity of colour. Such a mixture was made, assumed to be the proper tint for an equivalent of the ferric sulphocyanide, and employed as a standard. Mixtures were then made of three equivalents of sulphocyanide of potassium with one equivalent of the various ferric salts, each occupying 330 gr. meas. The standard red was then diluted till it was equal in colour to these several mixtures. The annexed table gives the different amounts of dilution required.

| | |
|---|----------------------|
| 1 eq. ferric nitrate + 3 eq. sulphocy. of potas. | 1700 gr. m. |
| 1 eq. ferric chloride + 3 eq. sulphocy. of potas. | 1900 gr. m. |
| 1 eq. ferric sulphate + 3 eq. sulphocy. of potas. | 2650 gr. m. |
| 1 eq. ferric acetate + 3 eq. sulphocy. of potas. | 7000 gr. m. (about). |

This affords us the elements requisite for a calculation of the actual amount of ferric sulphocyanide present in each of these mixtures; and had it been desirable, almost every observation given above might have been thus reckoned. The ratio between the volumes of the diluted standard ferric sulphocyanide, and that of any one of the other red mixtures (330 gr. meas.), gives the ratio between one equivalent and the fractional part existing in the said mixture. The four observations calculated on this principle give the following results:—

| | |
|--|---|
| 1 equiv. ferric nitrate + 3 equivs. sulphocyanide of potassium give | 0·1941 equivalent ferric sulphocyanide. |
| 1 equiv. ferric chloride + 3 equivs. sulphocyanide of potassium give | 0·1737 equivalent ferric sulphocyanide. |
| 1 equiv. ferric sulphate + 3 equivs. sulphocyanide of potassium give | 0·1245 equivalent ferric sulphocyanide. |
| 1 equiv. ferric acetate + 3 equivs. sulphocyanide of potassium give | 0·0471 equivalent ferric sulphocyanide (about). |

If this mode of reckoning involve no fallacy, the proportion between these four numbers should be the same as that given near

the commencement of this inquiry, where the colours produced on a different occasion by adding three equivalents of sulphocyanide of potassium to one equivalent of the ferric salts, were directly compared. That they do agree almost exactly will be seen from the following table, where column I. gives the numbers of the former experiment, and column II. those of the last calculation reduced to the same unit of comparison.

| | I. | II. |
|---|------|-------|
| 1 equiv. ferric nitrate + 3 equivs. sulphocyanide of potassium | 100 | 100 |
| 1 equiv. ferric chloride + 3 equivs. sulphocyanide of potassium | 89.4 | 89.5 |
| 1 equiv. ferric sulphate + 3 equivs. sulphocyanide of potassium | 65.2 | 64.2 |
| 1 equiv. ferric acetate + 3 equivs. sulphocyanide of potassium | 20 | 24.2? |

This close agreement proves not only the correctness of the two independent experiments, but also the correctness of this method of reckoning the amount of the coloured salt in any given mixture.

Influence of the mass of a substance present in the solution, but which is not one of the constituents of the coloured salt.—It has already been remarked that the addition of a colourless salt will reduce the colour of a solution of ferric sulphocyanide. The influence of mass in this kind of action remains to be examined.

A mixture was made of ferric sulphate and sulphocyanide of potassium. The red solution that resulted contained of course sulphate of potash. Successive portions of a solution of this salt were added, and the amount of decomposition effected was determined by means similar to those employed in previous experiments.

| Sulphate of potash added. | Water added to comparative solution. | Sulphate of potash added. | Water added to comparative solution. |
|----------------------------|--------------------------------------|-----------------------------|--------------------------------------|
| 5 measures = 22 measures. | | 30 measures = 92 measures. | |
| 10 measures = 38 measures. | | 40 measures = 115 measures. | |
| 15 measures = 52 measures. | | 60 measures = 155 measures. | |
| 20 measures = 67 measures. | | | |

This action then proceeds in a gradually decreasing ratio.

These very diversified experiments have put to a rigid test the truth of Berthollet's view. Whatever were the circumstances under which the reactions were tried, they invariably showed that the results were dependent both upon the nature and upon the quantity of all the substances in solution.

FERRIC GALLATE.

A solution of gallic acid was made of known strength. Equal portions of it were added to equal portions of the different ferric salts.

- 1 equivalent ferric nitrate with 1 equivalent gallic acid gave 100 parts of black salt.
- 1 equivalent ferric chloride with 1 equivalent gallic acid gave 88 parts of black salt.
- 1 equivalent ferric sulphate with 1 equivalent gallic acid gave 70 parts of black salt.
- 1 equivalent ferric citrate with 1 equivalent gallic acid gave 10? parts of black salt.

The mixture containing the citrate could not be accurately compared on account of its greenish hue. That made from the acetate was of an intense blue.

When single equivalents of nitrate of iron and gallic acid were mixed, a solution resulted in which the gallic acid had to such an extent combined with the sesquioxide of iron, that the addition of several equivalents of either one of the constituent substances caused a scarcely perceptible increase of colour.

The ferric chloride was then tried.

| Ferric chloride. | Gallic acid. | Black salt produced. | Ferric chloride. | Gallic acid. | Black salt produced. |
|----------------------|--------------|----------------------|----------------------|--------------|----------------------|
| 1 equiv. + 1 equiv. | | 88 | 1 equiv. + 4 equivs. | | 128 |
| 1 equiv. + 2 equivs. | | 108 | 1 equiv. + 6 equivs. | | 133 |
| 1 equiv. + 3 equivs. | | 120 | | | |

The citrate afforded a better opportunity of obtaining a numerical result representing the influence of the mass of one of the constituents.

| Ferric citrate. | Gallic acid. | Black salt produced. | Ferric citrate. | Gallic acid. | Black salt produced. |
|-----------------------|--------------|----------------------|-----------------------|--------------|----------------------|
| 1 equiv. + 5 equivs. | | 155 | 1 equiv. + 13 equivs. | | 297 |
| 1 equiv. + 7 equivs. | | 200 | 1 equiv. + 17 equivs. | | 353 |
| 1 equiv. + 9 equivs. | | 237 | 1 equiv. + 25 equivs. | | 445 |
| 1 equiv. + 11 equivs. | | 270 | 1 equiv. + 33 equivs. | | 509 |

Experiments were also tried with gallate of potash in the place of gallic acid.

1 eq. fer. nit. + 1 eq. gal. of pot. gave 100 parts of black salt.
 1 eq. fer. chl. + 1 eq. gal. of pot. gave 97 parts of black salt.
 1 eq. fer. sulph. + 1 eq. gal. of pot. gave 68 parts of black salt.
 1 eq. fer. citr. + 1 eq. gal. of pot. gave a blue solution.
 1 eq. fer. acet. + 1 eq. gal. of pot. gave a precipitate.

A mixture of single equivalents of gallate of potash and ferric nitrate gave nearly, but apparently not quite, the same depth of colour as when an equivalent of gallic acid was mixed with the same iron salt.

Ferric gallate was prepared by dissolving the hydrated sesquioxide of iron in gallic acid. It was divided into two equal parts, to one of which successive portions of hydrochloric acid were added, while the other was diluted after each addition till it had been reduced to the colour of the acid mixture.

| Hydrochloric acid added. | Water added to comparative solution. | Hydrochloric acid added. | Water added to comparative solution. |
|----------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| 1 measure = 3.4 measures. | | 3.25 measures = 10.1 measures. | |
| 2 measures = 6.6 measures. | | 4.5 measures = 12.0 measures. | |

It requires no further experiments to show that the ferric gallate bears the same testimony as the sulphocyanide.

FERRIC MECONATE.

Similar experiments were made with meconic acid and the iron salts. After mixing these substances, it was found necessary to

allow the solutions to stand a minute or two before observation, in order that the full colour might be developed.

1 eq. ferric nitrate + 1 eq. meconic acid (3HO , $\text{C}_{14} \text{H}_4 \text{O}_{14}$) gave 100 parts of red salt.

1 eq. ferric chloride + 1 eq. meconic acid (3HO , $\text{C}_{14} \text{H}_4 \text{O}_{14}$) gave 96 parts of red salt.

1 eq. ferric sulphate + 1 eq. meconic acid (3HO , $\text{C}_{14} \text{H}_4 \text{O}_{14}$) gave 72 parts of red salt.

1 eq. ferric citrate + 1 eq. meconic acid (3HO , $\text{C}_{14} \text{H}_4 \text{O}_{14}$) gave 42 parts of red salt.

1 eq. ferric acetate + 1 eq. meconic acid (3HO , $\text{C}_{14} \text{H}_4 \text{O}_{14}$) gave a red precipitate.

The influence of successive additions of meconic acid to a mixture of single equivalents of that substance and ferric nitrate was tried.

| Ferric nitrate. | Meconic acid. | Red salt produced. | Ferric nitrate. | Meconic acid. | Red salt produced. |
|----------------------|---------------|--------------------|----------------------|---------------|--------------------|
| 1 equiv. + 1 equiv. | | 88 | 1 equiv. + 4 equivs. | | 75 |
| 1 equiv. + 2 equivs. | | 80 | 1 equiv. + 6 equivs. | | 73 |
| 1 equiv. + 3 equivs. | | 76 | 1 equiv. + 8 equivs. | | 74 |

Here, instead of finding an increase of colour, as might have been expected by analogy, there is a distinct though small decrease. On examining the action more fully, and by repeated experiments, it was found that the maximum colour was obtained when the ferric nitrate and the meconic acid were mixed in single equivalents (or rather, in the proportion of 12 atoms of the former to 11 of the latter); that the addition of more ferric nitrate to such a mixture did not notably increase the colour; that the addition to it of 0.25 equivalent of meconic acid made little change; and that a greater addition caused a decided diminution of the tint.

A mixture of one equivalent of meconic acid with one equivalent of sesquichloride of iron was examined in a similar manner. The addition of meconic acid was found in this case also to diminish the colour. The effect of successive additions of the ferric salt was more particularly tried.

| Meconic acid. | Ferric chloride. | Red salt produced. | Meconic acid. | Ferric chloride. | Red salt produced. |
|------------------------|------------------|--------------------|-----------------------|------------------|--------------------|
| 1 equiv. + 1 equiv. | | 88 | 1 equiv. + 5 equivs. | | 99 |
| 1 equiv. + 1.2 equiv. | | 96 | 1 equiv. + 7 equivs. | | 93 |
| 1 equiv. + 1.8 equiv. | | 108 | 1 equiv. + 9 equivs. | | 99 |
| 1 equiv. + 2.6 equivs. | | 118 | 1 equiv. + 13 equivs. | | 119 |
| 1 equiv. + 3.8 equivs. | | 106 | | | |

It is evident that there is some action which twice changes the order of this series.

When ferric sulphate and meconic acid are mixed, it requires about seven atoms of the former to five of the latter to produce the greatest intensity of colour. It then just about equals in tint the mixture of five atoms of the ferric nitrate with the same amount of meconic acid, and made up to the same volume.

No amount of ferric citrate added to the above-mentioned amount of meconic acid is capable of bringing the colour up to that of the former mixtures.

These experiments were repeated with meconate of potash instead of the acid.

1 eq. fer. nitrate + 3KO, C₁₄ H₄ O₁₄ gave 100 parts of red salt.
 1 eq. fer. chloride + 3KO, C₁₄ H₄ O₁₄ gave 73 parts of red salt.
 1 eq. fer. sulphate + 3KO, C₁₄ H₄ O₁₄ gave 84 parts of red salt.
 1 eq. fer. citrate + 3KO, C₁₄ H₄ O₁₄ gave a trace of red salt.
 1 eq. fer. acetate + 3KO, C₁₄ H₄ O₁₄ gave a red precipitate.

These proportions differ considerably from those observed where meconic acid itself was employed.

The effect of successive additions of meconate of potash to the ferric nitrate was also tried.

| Ferric nitrate. | Meconate of potash. | Red salt produced. | Ferric nitrate. | Meconate of potash. | Red salt produced. |
|------------------------|---------------------|--------------------|-----------------------|---------------------|--------------------|
| 1 equiv. + 0.33 equiv. | | 34 | 1 equiv. + 1 equiv. | | 88 |
| 1 equiv. + 0.5 equiv. | | 50 | 1 equiv. + 1.2 equiv. | | 84 |
| 1 equiv. + 0.8 equiv. | | 74 | 1 equiv. + 1.5 equiv. | | 69 |

Here the greatest intensity of colour evidently occurs when about single equivalents are mixed, the addition of a larger quantity of meconate of potash producing a rapid diminution of the colour.

The same was observed in respect to the ferric chloride. When single equivalents had been mixed, the addition of more ferric salt was not found to make any great difference in colour. This action, however, was examined quantitatively by means of the citrate.

| Meconate of potash. | Ferric citrate. | Red salt produced. | Meconate of potash. | Ferric citrate. | Red salt produced. |
|------------------------|--------------------|-----------------------|------------------------|--------------------|-----------------------|
| 1 equiv. + 0·8 equiv. | | 97 | 1 equiv. + 3·8 equivs. | | 102 |
| 1 equiv. + 1·2 equiv. | | 80 | 1 equiv. + 5 equivs. | | 125 |
| 1 equiv. + 1·8 equiv. | | 69 | 1 equiv. + 7 equivs. | | 154 |
| 1 equiv. + 2·6 equivs. | | 74 | 1 equiv. + 9·2 equivs. | | 165 |

Imagining that the rapid decrease of colour manifested when meconate of potash was added in excess to the ferric salt, might be due to the formation of some paler double compound, I added the potash salt to a solution of pure meconate. The colour was greatly diminished.

These results show satisfactorily enough that the amount of meconate of iron formed depends upon the nature of the various substances in solution; but their testimony in respect to the mass of these substances is obscured by the formation of these double compounds. Thinking to avoid this by always using the same amount of meconic acid and iron, and yet to exhibit the effect of mass, the following experiments were performed. Pure meconate of iron was treated with acetate of potash; it was quickly reduced to a pale yellow. Oxalate or phosphate of potash had the same effect. A strong solution of sulphate of soda was tried: —

| Sulphate of soda added. | Water added to comparative solution. | Sulphate of soda added. | Water added to comparative solution. |
|----------------------------|--|----------------------------|--|
| 5 measures = 16 measures. | | 40 measures = 58 measures. | |
| 10 measures = 26 measures. | | 60 measures = 80 measures. | |
| 20 measures = 36 measures. | | | |

Another solution of meconate of iron was similarly treated with dilute hydrochloric acid: —

| Hydrochloric acid added. | Water added to comparative solution. | Hydrochloric acid added. | Water added to comparative solution. |
|-----------------------------|--|-----------------------------|--|
| 2 measures = | 3.6 measures. | 7 measures = | 15 measures. |
| 3 measures = | 5 measures. | 9 measures = | 20 measures. |
| 5 measures = | 10 measures. | | |

It is evident, that although a reduction of the amount of ferric meconate always takes place, there is some cause interfering with the regularity of the decrease of colour.

The amount of ferric meconate depends, therefore, upon the nature and upon the quantity of all the substances present at the same time in the solution; but the regularity of the action of mass, which was observed with the sulphocyanide and gallate, is not confirmed in this instance.

FERRIC PYROMECONATE.

Thinking that the irregularity in the influence of mass might be more or less connected with the tribasic character of meconic acid, it occurred to me that an examination of ferric pyromeconate would be desirable, since pyromeconic acid is monobasic, and yet strikes an intense red with the sesquioxide of iron, and in many other respects resembles the substance from which it is derived.

- 1 equivalent ferric nitrate + 3 equivalents pyromeconic acid gave 100 parts of red salt.
- 1 equivalent ferric chloride + 3 equivalents pyromeconic acid gave 86 parts of red salt.
- 1 equivalent ferric sulphate + 3 equivalents pyromeconic acid gave 39 parts of red salt.
- 1 equivalent ferric citrate + 3 equivalents pyromeconic acid gave 27 parts of red salt.
- 1 equivalent ferric acetate + 3 equivalents pyromeconic acid gave a red precipitate.
- 1 equivalent ferric nitrate + 3 equivs. pyromeconate of potash gave 100 parts of red salt.
- 1 equivalent ferric chloride + 3 equivs. pyromeconate of potash gave 74 parts of red salt.
- 1 equivalent ferric sulphate + 3 equivs. pyromeconate of potash gave 36 parts of red salt.
- 1 equivalent ferric citrate + 3 equivs. pyromeconate of potash gave 26 parts of red salt.
- 1 equivalent ferric acetate + 3 equivs. pyromeconate of potash gave a red precipitate.

On trying the influence of mass, it was found that the addition of pyromeconic acid rapidly *diminished* the colour of ferric pyromeconate; and that the colour was the deepest when the base was in large excess.

Thinking that the effect of a colourless salt upon the red pyromeconate might display more clearly the influence of mass, a mixture of ferric chloride and pyromeconic acid was experimented on with a solution of sulphate of potash:—

| Sulphate of potash added. | Water added to comparative solution. | Sulphate of potash added. | Water added to comparative solution. |
|--------------------------------|--|------------------------------|--|
| 3.7 measures = 12.5 measures. | | 20 measures = 37.5 measures. | |
| 11.2 measures = 27.5 measures. | | 30 measures = 47.5 measures. | |

The monobasic pyromeconate appears, therefore, to be similar in its testimony to the tribasic meconate.

FERRIC ACETATE.

Twelve equivalents of acetate of potash were added to one equivalent of each of the ferric salts, and gave the following proportions:—

1 equivalent ferric nitrate + 12 equivalents acetate of potash gave
100 parts of red salt.

1 equivalent ferric chloride + 12 equivalents acetate of potash gave
139 parts of red salt.

1 equivalent ferric sulphate + 12 equivalents acetate of potash gave
112 parts of red salt.

1 equivalent ferric citrate + 12 equivalents acetate of potash gave
no red salt.

These proportions differ greatly from those which have been previously observed.

The effect of successive additions of acetate of potash was tried:—

| Ferric nitrate. | Acetate of potash. | Red salt produced. | Ferric nitrate. | Acetate of potash. | Red salt produced. |
|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| 1 equiv. + 3 equivs. | | 88 | 1 equiv. + 21 equivs. | | 87 |
| 1 equiv. + 6 equivs. | | 109 | 1 equiv. + 30 equivs. | | 64 |
| 1 equiv. + 9 equivs. | | 109 | 1 equiv. + 39 equivs. | | 61 |
| 1 equiv. + 12 equivs. | | 102 | 1 equiv. + 48 equivs. | | 52 |
| 1 equiv. + 15 equivs. | | 96 | 1 equiv. + 63 equivs. | | 46 |

Here, again, as in the case of the meconate, there is something producing a great irregularity of action.

To a mixture of one equivalent of ferric nitrate, and three of acetate of potash, successive portions of the iron salt were added. They rendered the mixture much paler, reducing it at last almost to the colour of the nitrate itself.

In order to ascertain whether these changes of colour were due to the formation of double salts containing both iron and potash, three equal portions of the ferric acetate employed in the previous experiments were treated respectively with solutions of acetate of potash, acetic acid, and water. The potash salt caused a slight *increase* of colour, and the pure acid a great *decrease*, as compared with the effect of mere dilution. It is clear that there exist different combinations of acetic acid and sesquioxide of iron; indeed, it has been observed before by others, that a highly coloured solution of ferric acetate will spontaneously deposit red oxide and become almost colourless.

The ferric acetate, then, confirms Berthollet's view, but, like the meconate, its testimony in respect to the influence of the mass is equivocal.

FERRIC FERROCYANIDE.

The ferric ferrocyanide, although insoluble in pure water, is soluble in the presence of oxalic acid, giving a deep blue. A mixture was made of a known amount of ferrocyanide of potassium with that acid, and it was added to the various ferric salts. The blue from the nitrate, chloride, or sulphate was very intense; the mixture containing the acetate was colourless the first minute, but gradually became blue; while that containing the citrate also deepened in tint on standing. After remaining about two hours, the coloured mixtures were in the following proportions:—

- 1 equiv. ferric nitrate + 3 equivs. ferrocyanide of potassium gave 100 parts of blue salt.
- 1 equiv. ferric chloride + 3 equivs. ferrocyanide of potassium gave 87 parts of blue salt.
- 1 equiv. ferric sulphate + 3 equivs. ferrocyanide of potassium gave 89 parts of blue salt.
- 1 equiv. ferric acetate + 3 equivs. ferrocyanide of potassium gave 45 parts of blue salt.
- 1 equiv. ferric citrate + 3 equivs. ferrocyanide of potassium gave 60 parts of blue salt.

The effect of mass was also tried. The addition of more ferrocyanide of potassium to a mixture of one equivalent of ferric

nitrate and three of the ferrocyanide produced no appreciable increase of colour. With the citrate, however, the following numerical results were obtained:—

| Ferric citrate. | Ferrocyanide of potassium. | Blue salt produced. | Ferric citrate. | Ferrocyanide of potassium. | Blue salt produced. |
|----------------------|----------------------------|---------------------|-----------------------|----------------------------|---------------------|
| 1 equiv. + 3 equivs. | | 88 | 1 equiv. + 9 equivs. | | 113 |
| 1 equiv. + 6 equivs. | | 107 | 1 equiv. + 15 equivs. | | 120 |

Acetate or citrate of potash added to a mixture of ferric nitrate and ferrocyanide of potassium in oxalic acid, produces no perceptible change at the moment of mixing; but a decrease of colour becomes apparent after a few minutes, and continues, becoming more and more marked for some hours.

The ferrocyanide then bears a similar testimony to the truth of Berthollet's position to what the ferric sulphocyanide and galate do.

FERRIC COMENAMATE.

Single equivalents of comenamic acid ($C_{12}H_5NO_8 + 4HO$) were mixed with single equivalents of the different ferric salts. With the nitrate, chloride, and sulphate it gave a most intense purple, with the citrate a wine-red solution, and with the acetate a precipitate.

The three purple solutions were about equally deep in colour; they were unaffected by the addition of any amount of iron salt, but were reddened by the addition of comenamic acid. The mixture containing the citrate was uninfluenced in the character of the tint, and almost so in the depth of it, by the addition of any amount of either the acid or the iron salt. It was quite evident from this, that comenamic acid has a great tendency to combine with sesquioxide of iron in place of water, and that it is capable of forming two distinct compounds. Indeed, it was found that one equivalent, or less, of comenamic acid uniformly gave with one equivalent of nitrate of iron a deep bluish-purple compound; and that two equivalents, or more, gave a wine-red compound; whilst any proportion intermediate between one and two equivalents gave an intermediate tint.

Comenamate of potash and of ammonia gave similar results to comenamic acid itself; but the colour produced with the citrate at least was not so deep. The following were the ratios:—

1 equivalent ferric citrate + 1 equivalent comenamic acid gave
5 parts of red salt.

1 equivalent ferric citrate + 1 equivalent comen. of ammonia gave
4 parts of red salt.

1 equivalent ferric citrate + 1 equivalent comen. of potash gave
2.9 parts of red salt.

The addition of citrate of iron to a mixture of single equivalents of it and comenamate of potash caused an increase of colour, but no amount turned the solution purple.

Comenamic acid, then, is able to overcome the great affinity of citric acid for ferric oxide only so far as to produce the more acid salt. The purple comenamate was reddened instantly by citrate of potash, yet a large addition of that substance did not wholly destroy the colour.

That comenamic acid has not so great an affinity for sesquioxide of iron as to be unaffected by the presence of nitric, hydrochloric, or sulphuric acid, was easily demonstrated. The following experiment illustrates the action of such a substance. To a solution consisting of single equivalents of ferric chloride and comenamic acid, successive portions of hydrochloric acid were added. The original mixture was bluish-purple.

| Hydrochloric acid added. | Colour of mixture. |
|--------------------------|---|
| 3 measures. | Bluish purple, but paler by an amount equiv. to 25 measures of water. |
| 6 measures. | Bluish purple, but paler by an amount equiv. to 40 measures of water. |
| 9 measures. | Bluish purple, but paler by an amount equiv. to 54 measures of water. |
| 15 measures. | Visibly redder, and paler by an amount equiv. to 80? measures of water. |
| 21 measures. | Red purple. |
| 31 measures. | Pink. |
| 55 measures. | Still perceptibly pink. |

The affinity, then, of comenamic acid for sesquioxide of iron, though very great, is influenced both by the nature and by the quantity of other substances present in the same solution.

FERRIC BROMIDE.

Experiments were also made on the ferric bromide. The iron salts were employed without dilution, as the bromide itself is but little redder than the chloride. Three equivalents of hydrobromic

acid added to one of ferric nitrate produced a distinct red ; added to the ferric citrate, they produced little change in the colour. Yet the bromine has evidently a great tendency to combine with the iron ; for, though the addition of a larger quantity of hydrobromic acid to the nitrate did perceptibly increase the colour, a maximum effect seemed attained when only about twelve equivalents were added. The addition of twelve equivalents in the case of the citrate produced likewise a red tint similar to that from the nitrate. Bromide of potassium did not redden the ferric citrate. Numerical results could not be obtained on account of the paleness of the colour.

THE FERRIC SALTS IN GENERAL.

Effect of mass of solvent.—In connection with these experiments on ferric salts, it became a matter of interest to ascertain whether changes in the mass of water itself had any influence on the composition of the salts contained in these coloured solutions.

The only methods which occurred to me of obtaining an answer to this inquiry, were, to ascertain whether dilution caused any greater or less decrease of colour in some substances than in others of the same tint ; and whether the decrease of colour by dilution was uniform in the same salt, by whatever mixture it might be produced.

It has frequently been noticed that a red solution of ferric sulphocyanide is reduced by the addition of water more than the simple dilution seemed capable of accounting for, and more than the red meconate is.

To ascertain whether this is really the case, two solutions, the one of ferric sulphocyanide, the other of ferric meconate, were made up to the same depth of colour and the same volume, each occupying 200 grain measures ; they were then equally diluted :

| | |
|---|------------------------------|
| 200 gr. m. of the sulphocyanide equalled in colour | 200 gr. m. of the meconate. |
| 400 gr. m. of the sulphocyanide equalled in colour | 730 gr. m. of the meconate. |
| 720 gr. m. of the sulphocyanide equalled in colour | 2460 gr. m. of the meconate. |
| 1440 gr. m. of the sulphocyanide equalled in colour | 7540 gr. m. of the meconate. |

The disparity here is very great, and takes place at an increasing ratio.

It seemed desirable to test, if possible, whether this diversity was due entirely to the sulphocyanide, or whether the meconate

might not also be departing from the ratio of decrease in colour which mere dilution would cause. For this purpose, five solutions were taken of equal bulk and of the same depth of colour. They consisted respectively of meconate of iron, a mixture of ferric chloride and sulphocyanide of potassium, port wine and water, red ink, and infusion of cochineal. These solutions, though not identical in colour, were sufficiently near for the purpose. On repeated dilution of each with equal amounts of water, they all retained the same colour relatively, except the sulphocyanide, which became yellowish and much lighter.

It may fairly be concluded, then, without predicting anything as to the action of water on dry salts, that large quantities of water have no specific action on meconate of iron, but that in some way they affect the sulphocyanide. Is this a mere physical effect upon the particular colour; or does some change take place in the composition of the salt itself? In order to test whether this action of water was influenced by the presence of other substances, red solutions of equal volume and equal depth of colour were prepared by the following admixtures:—ferric chloride with sulphocyanide of potassium in large excess; sulphocyanide of potassium with ferric chloride in large excess; ferric nitrate with sulphocyanide of potassium; the same salts with the addition of a large quantity of sulphate of potash; sulphocyanide of potassium with ferric acetate; ferrous and ferric sulphocyanide with sulphocyanide of lead; and nearly pure sesquisulphocyanide of iron. On repeated dilution with equal amounts of water, these all appeared to retain the same relative colour.

It seems, then, as far as this experiment can prove it, that the action of water, whatever it be, is exerted equally upon red sulphocyanide of iron, with whatever other substance it may be mixed. This removes any doubt that might have rested from this cause on some of the original experiments with ferric sulphocyanide: and the fact that those experiments were always comparative, leaves little ground for any possible objection.

An experiment was likewise tried in order to determine whether the presence of other substances had any influence in the dilution of meconate of iron. Solutions were taken of pure ferric meconate, and of mixtures of ferric chloride with meconic acid; of the same with meconate of potash, both in large excess and otherwise; of ferric nitrate with meconic acid; of the same with meconate of potash; and of ferric citrate with meconic acid. On repeated dilution with equal amounts of water, no notable difference was observed in the relative depths of colour of these several solutions, except in the case of the citrate, which, on standing for some hours after dilution, lost colour considerably. The red also, was of a more pure crimson where there was nitric acid.

Pyromeconate of iron prepared by double decomposition was affected in colour by dilution in a similar manner to the meconate. Water, too, seemed to have the same effect on the blue ferrocyanide as on ammoniacal sulphate of copper. In these cases, however, the salts compared were not of precisely the same tint.

Relative strength of affinity.—Having considered the evidence borne by eight coloured and soluble ferric salts as to the truth of certain views of the laws that regulate chemical combination, we have found their testimony on the main points uniform. We may now go further, and by examining the results above given determine the relative degree of affinity exerted by the different acids for sesquioxide of iron as compared with potash.

The following is the order of affinity of the different acids experimented with for sesquioxide of iron and an equivalent amount of potash:—

Least affinity for sesquioxide of iron as compared with potash.

| | | |
|------------------------|-----------|-------|
| Hydrosulphocyanic acid | | 1 |
| Nitric acid | | 4 |
| Hydrochloric acid | | 5 |
| Sulphuric acid | | 7 |
| Gallic acid | | 10 ? |
| Pyromeconic acid ? | | |
| Meconic acid ? | | |
| Acetic acid | | 20 ? |
| Hydrobromic acid | | |
| Comenamic acid | | |
| Citric acid | | 100 |
| Hydroferrocyanic acid | | 170 ? |

Greatest affinity for sesquioxide of iron as compared with potash.

The numbers in the preceding table are deduced from the experimental data, but they must be considered as only rough approximations to the truth. The notes of interrogation indicate that the means of determination were themselves open to doubt.

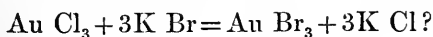
Effect of differences of temperature.—The experiments narrated in this paper were all performed at the ordinary temperature. The slight changes that may have taken place in that respect from one day to another were incapable of affecting visibly the coloured solutions. Much greater variations had a perceptible effect, but whether this ever arose from changes in the balance of affinities I am not prepared to say.

I now pass on to consider the testimony borne by other coloured salts, not ferric compounds, in respect to the question at issue.

GOLD SALTS.

The bromide of gold is of an intense scarlet, whilst the chloride is of a yellow colour.

Pure chloride of gold free from hydrochloric acid was prepared. To a portion of this, three equivalents of bromide of potassium were added. The formation of the scarlet terbromide of gold was so complete, that the addition of either of the salts employed caused, singly, too small an increase of colour to be readily appreciated. Is it to be considered, then, that the decomposition in this case has been complete? may it be represented thus—



This was more rigidly tested by adding chloride of potassium in large excess to bromide of gold.

| Strong chloride of potassium added. | Water added to comparative solution. | Strong chloride of potassium added. | Water added to comparative solution. |
|---|--|---|--|
| 5 measures = 30 measures. | | 35 measures = 105 measures. | |
| 10 measures = 48 measures. | | 50 measures = 135 measures. | |
| 20 measures = 70 measures. | | 75 measures = 180 measures. | |

Some difficulty was felt in determining the last numbers of this experiment, from the fact that the chloride of potassium had by its great excess converted nearly the whole of the bromide of gold into the yellow chloride, or still paler double chloride.

It was found that bromide of gold was reduced in colour by very small quantities of hydrochloric acid, or even of the common yellow crystals of the chloride of gold, which are, as is well known, the hydrochlorate of that salt.

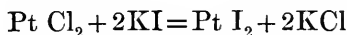
These gold salts, then, have afforded a good example of the influence of mass in gradually counterbalancing and overcoming a strong affinity.

PLATINUM SALTS.

Neutral bichloride of platinum and different amounts of iodide of potassium were mixed in a series of vessels, diluted to an equality of bulk, and allowed to stand some hours for the colour to develop itself properly — a precaution which in this instance was necessary. The following were the appearances noted: —

| Bichloride of platinum. | Iodide of potassium. | Character of mixture. |
|-------------------------|----------------------|--|
| 1 equiv. + 0.5 equiv. | | Very pale brown solution. |
| 1 equiv. + 1 equiv. | | Reddish brown, and opalescent. |
| 1 equiv. + 2 equivs. | | The same, but deeper. |
| 1 equiv. + 3 equivs. | | The same; some biniodide of platinum deposited on the glass. |
| 1 equiv. + 4 equivs. | | Red; opalescence slight; biniodide of platinum deposited. |
| 1 equiv. + 6 equivs. | | Bright red; scarcely any opalescence or deposit. |
| 1 equiv. + 8 equivs. | | Brighter red; no opalescence or deposit. |
| 1 equiv. + 10 equivs. | | Still brighter red. |
| 1 equiv. + 15 equivs. | | Still brighter. |

The formation of the insoluble iodide of platinum renders some of these cases less distinct in their testimony than the instances previously considered. The opalescence, too, was doubtless owing to a minute trace of solid matter. This, however, is perfectly clear, that the two salts, though they have mutually decomposed each other, have not done so in the atomic proportions; not according to the schemes



and



It has required, in fact, about four equivalents of iodide of potassium to produce the maximum amount of the platinic iodide; and the latter terms of the series exhibit a still increasing amount of the intensely red double iodide of platinum and potassium. It may be expected that the double chloride is one of the salts produced in such a mixture. Successive additions of a strong solution of chloride of potassium to a mixture of one equivalent of bichloride of platinum with two of iodide of potassium, were found to reduce the colour greatly, making it browner.

COPPER SALTS.

Soluble copper salts are, I believe, all of a blue colour when dissolved in a large amount of water; but a strong solution of the chloride, and of one or two others, is green. It has frequently been observed, that on the addition of strong hydrochloric acid to a concentrated solution of sulphate of copper, a green colour takes the place of blue; and it has been naturally concluded that

chloride of copper was then formed. This reaction was likewise investigated.

| Sulphate of copper. | Hydrochloric acid. | Colour of mixture. |
|------------------------|-----------------------|------------------------------|
| 1 equiv. + | 1 equiv. | Blue. |
| 1 equiv. + | 2 equivs. | Blue, with a tinge of green. |
| 1 equiv. + | 3 equivs. | Dull green. |
| 1 equiv. + | 4 equivs. | Dull green. |
| 1 equiv. + | 6 equivs. | Bright green. |
| 1 equiv. + | 8 equivs. | Bright green. |
| 1 equiv. + | 16 equivs. | Very bright green. |

From this it is evident that single equivalents of sulphate of copper and of hydrochloric acid are not resolved wholly (nor indeed to any great extent) into chloride of copper and sulphuric acid; and that the relative mass of the two substances influences the result.

In order to observe the influence of the mass of water, the following experiments were instituted. Eight portions were taken of a saturated solution of sulphate of copper at 60° F., and were mixed with progressively increasing amounts of strong hydrochloric acid solution. The colours produced were noted. They are given in column I. of the subjoined table. Each of the mixtures was then diluted with half its volume of water. The resulting shades are given in column II. Column III. represents the shades when the water was doubled; column IV. when the solutions were of three times their original volume:—

| Sulph. cop. sol. | Hydroch. ac. sol. | I. | II. | III. | IV. |
|---------------------|----------------------|-------------------|-------------------------------|--|---------------------------------|
| 50 mea. + 10 mea. | | Perfectly blue. | Perfectly blue. | As Column II., but all paler and more blue. | Pure blue. |
| 50 mea. + 12·5 mea. | | Greenish blue. | Blue. | | Pure blue. |
| 50 mea. + 15 mea. | | Distinctly green. | Blue, with trace of green. | | Pure blue. |
| 50 mea. + 20 mea. | | Clear green. | Just a shade greener. | | Pure blue. |
| 50 mea. + 30 mea. | | Bright green. | Dull bluish green. | | Pure blue. |
| 50 mea. + 40 mea. | | Bright green. | Green | | Blue, with a trace of green. |
| 50 mea. + 50 mea. | | Brighter green. | Green | | Blue, with a trace of green. |
| 50 mea. + 70 mea. | | Still brighter. | Green | | Blue, with a trace of green. |

It is not to be inferred that the sulphate of copper was in larger quantity in column IV. than in column I., for water acts according to its mass upon pure chloride of copper, converting it from green into a blue compound.

To seven portions of the standard solution of sulphate of copper, each measuring 50 parts, were added respectively 10, 20, 30, 40, 50, 70, and 100 parts of a saturated solution of chloride of sodium. There resulted a series of tints passing gradually from blue to almost pure green, without any sudden transition.

A strong solution of chloride of zinc added to a solution of sulphate of copper, also produced a greenish colour, which increased as more chloride was added.

Knowing the disposition of oxide of lead and acetic acid to combine, it occurred to me that chloride of lead might decompose the acetate of copper very readily. Accordingly, two equal portions of the blue acetate were mixed with equivalent amounts of chloride of lead and chloride of sodium in solution; and it was indeed found that the former caused a greater diminution of the colour than the latter did. In this experiment, much water was necessarily employed, but chloride of copper always gives a far paler blue solution than an equivalent amount of the acetate does.

These reactions with copper salts bear additional testimony, therefore, to the truth of the previous views.*

MOLYBDOUS SALTS.

As the molybdous fluoride gives a purple, and the chloride a green solution, these salts offered another means of testing whether complete or partial decomposition ensued on the mixing of binary compounds. Molybdous oxide was dissolved in hydrofluoric acid, and the resulting purple solution was treated with hydrochloric acid. It changed gradually to a greenish blue; and, on adding more hydrochloric acid, to a positive green. Time entered as an appreciable element into this change.

The converse of this experiment was also tried. The molybdous oxide dissolved in hydrochloric acid of a green colour. The addition of hydrofluoric acid to this gave at the first moment a rich

* After this paper had been read, the following note was added:—Changes in the state of combination of an element may be rendered visible by a change in the intensity of a colour, even where no change in its character occurs. Thus oxide of copper dissolved in acetic acid gives a much more intense blue than when the same amount is dissolved in sulphuric acid. This fact was taken advantage of in the following experiment, which affords additional evidence of the truth of my main deduction. Sulphuric acid was added to a solution of acetate of copper; it reduced the colour greatly. The experiment was reversed, acetic acid being added to a solution of sulphate of copper; it deepened the colour, but considerable excess of the acid was required to make a very evident difference.

purple, which was immediately succeeded by a white precipitate, insoluble in any excess of hydrofluoric acid, but readily soluble in hydrochloric acid with reproduction of the green.

MANGANESE SALTS.

Intermediate between the protoxide of manganese and the non-basic oxides, there exists a brownish-red salifiable compound, of the formula Mn_3O_4 . It is described in Gmelin's Handbook under the designation "manganoso-manganic oxide." Its solution in hot phosphoric acid or cold oil of vitriol is red, but it dissolves in other acids with a deep brown colour.

I prepared the sulphate and hydrochlorate of this base, and found that the addition of hydrochloric acid in excess caused a change in the colour of the sulphate from red to reddish brown, and eventually brown; while, on the other hand, the addition of sulphuric or phosphoric acid in excess to a solution of the brown chloride converted it into the red salt. Thus it appears that the oxide in question has no such affinity for either one of these acids, but that it is displaced more or less by the other.

BLUE GALLATE OF IRON.

Gallic acid, when added to iron salts, is apt to strike a deep blue colour, from the formation of a very stable compound of the organic acid with both the basic oxides of iron at once.

A blue solution was prepared by mixing solutions of gallic acid and of green vitriol that had been exposed to the air. The effect of sulphuric acid was tried.

| Sulphuric acid added. | Water added to comparative solution. | Sulphuric acid added. | Water added to comparative solution. |
|---------------------------|--------------------------------------|-----------------------------|--------------------------------------|
| 1 measure = 9 measures. | | 10 measures = 63 measures. | |
| 2 measures = 18 measures. | | 14 measures = 105 measures. | |
| 4 measures = 34 measures. | | 16 measures = 136 measures. | |
| 6 measures = 46 measures. | | 18 measures = 174 measures. | |
| 8 measures = 55 measures. | | 20 measures = 204 measures. | |

This experiment suffices to prove the influence upon the production of this blue gallate, both of the nature and quantity of other substances present in the solution at the same time.

QUININE SALTS.

In his elaborate paper "On the Change of Refrangibility of Light,"* Professor Stokes has shown that various acid salts of quinine exhibit that remarkable internal dispersion of light which is now known by the name "fluorescence." He mentions the acid sulphate, phosphate, nitrate, acetate, citrate, tartrate, oxalate, and hydrocyanate, as giving rise to the phenomenon; while quinine dissolved in hydrochloric acid did not present any such appearance. He found, moreover, that the addition of hydrochloric acid, or chloride of sodium, to one of the fluorescent salts destroyed the colour. Hence he concluded, and no doubt correctly, that in these cases muriate of quinine was formed; and to obviate the objection that possibly the non-fluorescent salt in solution might be a sort of double salt, in which the quinine was combined with the hydrochloric and the other acid in atomic proportion, he devised the following elegant experiment. To a strong warm solution of neutral sulphate of quinine, which displays no fluorescence, a very small quantity of hydrochloric acid was added; it produced the blue appearance: more hydrochloric acid was added; the blue was destroyed. This seemed intelligible only on the supposition that the small quantity of acid first added displaced an equivalent amount of sulphuric acid, which, combining with the undecomposed sulphate, formed the acid salt which displays fluorescence to such a remarkable degree; and that the larger quantity of hydrochloric acid decomposed this again, setting free the sulphuric acid, and leaving the quinine in solution as hydrochlorate.

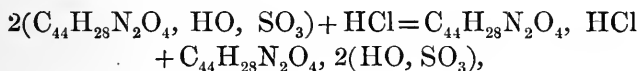
From the manner in which Professor Stokes describes and comments on these experiments, it is evident that he imagined (as most others would have done) that the decomposition was perfect, and that, in the particular experiment just mentioned, every particle of the quinine existed in the solution in the form of hydrochlorate, on account of the stronger affinity of that acid for the base. He states, moreover, that "even sulphuric acid is incapable of developing the blue colour in a solution of quinine in hydrochloric acid." If this be true, it evidently militates against the conclusions that double decomposition does not take place perfectly in solution, unless aided by the insolubility or volatility of one or more of the compounds produced, and that great mass counterbalances weak affinity. Accordingly, I repeated the experiments *quantitatively*, and performed some additional ones.†

* Philosophical Transactions, 1852.

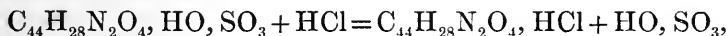
† Since writing the above, my attention has been drawn to a paragraph in Professor Stokes's second paper (Philosophical Transactions for 1853, p. 394.), in which he remarks that the neutral hydrochlorate of quinine is not absolutely non-fluorescent, as first stated, and that the hydrocyanate is like the hydrochlorate.

| Sulphate of quinine. | Hydrochloric acid. | Character of fluorescence. |
|-----------------------|--------------------|---|
| 1 equiv. + 0.5 equiv. | | A deep blue entering far into the liquid. |
| 1 equiv. + 1 equiv. | | A more intense blue, and confined to the edges. |
| 1 equiv. + 1.5 equiv. | | Much as the preceding. |
| 1 equiv. + 2 equivs. | | Rather fainter blue. |
| 1 equiv. + 3 equivs. | | Decreasing. |
| 1 equiv. + 4 equivs. | | Still decreasing. |
| 1 equiv. + 6 equivs. | | Fainter. |
| 1 equiv. + 8 equivs. | | Still fainter. |
| 1 equiv. + 12 equivs. | | Very faint. |
| 1 equiv. + 20 equivs. | | Just visible. |
| 1 equiv. + 30 equivs. | | As above. |
| 1 equiv. + 50 equivs. | | Invisible except under the most favourable circumstances. |

It will be seen at once, that the double decomposition between the sulphate of quinine and the hydrochloric acid was not perfect. Had it been so, the first line of the experiment would have been represented by the formula —



and the largest possible amount of fluorescence would have been obtained: while the second line would have been according to the formula —



and there would have been no fluorescence visible with this or any higher proportion of hydrochloric acid. But instead of single equivalents of sulphate of quinine and hydrochloric acid giving a non-fluorescent mixture, the blueness was only then attaining its maximum. Chloride of sodium was found to have even less power of decreasing the blue colour than an equivalent amount of the acid has.

Neutral hydrochlorate of quinine was prepared. Its solution diluted showed a mere trace of blue, which was removed on the addition of a drop or two of free hydrochloric acid. Portions of this solution were mixed with all the acids mentioned by Stokes as giving fluorescent compounds with quinine. The addition of

sulphuric, nitric, phosphoric, acetic or oxalic acid, instantly reproduced the blue colour in a very marked manner. Citric or tartaric acid added in very large excess also produced the blue, but it was faint. I failed to detect any change on the addition of a considerable amount of hydrocyanic acid.

Similarly, a solution of sulphate of soda in considerable excess was added to an acid solution of hydrochlorate of quinine. A very perceptible amount of blue made its appearance. This also is in perfect consonance with what might theoretically be expected, and indicates that not only had the commixture of sulphate of soda converted a portion of the hydrochlorate of quinine into sulphate, but the free hydrochloric acid had decomposed some of the sulphate of soda, liberating sulphuric acid, which had combined with the quinine salt to form the bisulphate. That a mixture of neutral sulphate of quinine with sulphate of soda does not give the blue tint, unless some free acid be added, was verified by previous experiment.

Stokes also states that iodide or bromide of potassium added to a solution of bisulphate of quinine, or the acid phosphate, destroys the fluorescence. On examining these reactions, I found that these haloid salts behaved precisely as the chloride did.

This accumulation of evidence all goes to prove that quinine follows the same laws as the substances previously considered.

COMPOUND ETHERS.

Compound ethers may be regarded as organic salts in which certain compound radicals take the place of metals, and it is to be expected that they will follow the same general laws as the binary compounds that have been previously examined. Their insolubility in water precludes the use of aqueous solutions of the substances intended to act upon them; but alcohol affords a convenient medium for the reaction; and when this is employed, results are obtained which are perfectly analogous to those already described in the case of different metallic salts. The following experiment may be taken as an example. A large excess of oxalic acid was dissolved in alcohol along with acetic ether, warmed, and allowed to stand for some hours. The mixture was then submitted to gentle distillation, and there passed over acetic ether mixed with alcohol and with oxalic ether. The oxalic acid had therefore displaced a certain amount of acetic acid; but though it existed in such large excess that it began to crystallise out, it had not displaced the whole.

GENERAL INFERENCES FROM THE PRECEDING EXPERIMENTS.

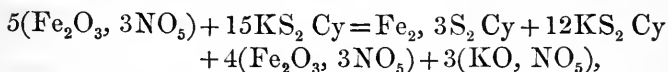
The concurrent testimony of the diversified experiments here detailed is in favour of the view, that when two binary compounds are mixed in solution, there ensues a partition of the two electro-positive between the two electro-negative elements, according to certain proportions regulated both by the difference of strength in the affinities, and by the relative quantities of the different bodies. The reverse of this does indeed appear at first sight to be the case in certain instances; as for instance when equivalent portions of sulphocyanide of potassium and ferric citrate are mixed, or of chloride of gold and bromide of potassium. But it makes all the difference whether there be a small, though inappreciable, quantity of the other salt formed at the same time, or whether the decomposition be absolute; and a consideration of the whole series of experiments, and of the influence of mass in these very instances, will leave, I think, a strong conviction on the mind that such cases differ from the others only in degree, and that if we possessed the means of observing minuter differences of colour we should find evidence of traces of the original salts still remaining. But of this each reader will form his independent judgment. Among those instances where evidently four salts were produced by the mixture of two, the following substances took part in the reaction:—

Iron (in both basic conditions), gold, platinum, mercury, copper, zinc, lead, molybdenum, manganese, baryta, lime, potash, soda, ammonia, hydrogen, ethyl, quinine.

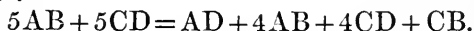
Sulphuric, nitric, phosphoric, hydrochloric, hydrobromic, hydriodic, hydrofluoric, hydrosulphocyanic, hydroferrocyanic, acetic, oxalic, citric, tartaric, gallic, meconic, pyromeconic, and come-namic acids.

It must be borne in mind, that when, in studying the mutual action of AB and CD, we have determined the laws according to which A and D combine, we have equally ascertained them in reference to C and B; that is to say, to take a particular instance, if we find, on mixing ferric nitrate and sulphocyanide of potassium, that ferric sulphocyanide is formed in certain proportions according to the relative force of affinity and mass, we have determined this also in respect to the nitric acid and the potash. We know, indeed, that for every portion of ferric sulphocyanide produced, an exactly equivalent portion of nitrate of potash must be formed. And not only this, but in any such mixture, where we know the original amounts of the two salts, and the amount of any one of the four into which they are resolved, we have the data for determining the amounts of the other three likewise. Suppose (which is about the truth) that one equivalent of ferric nitrate mixed with

three equivalents of sulphocyanide of potassium produce one-fifth of an equivalent of ferric sulphocyanide, the following is the only formula which can represent the reaction. The amounts are multiplied by five to avoid decimals:



or more simply,



Of course this method of reckoning is inapplicable where poly-basic acids are concerned.

TESTIMONY FROM OTHER CHEMICAL PHENOMENA.

There are many chemical phenomena, beside those connected with colour, which bear testimony respecting the question whether two salts in solution resolve themselves into four.

The testimony of precipitation.—The idea that when double decomposition occurs, the acids and bases make a perfect exchange, arose doubtless from what is constantly observed when a precipitate ensues. In that case A combines wholly with D, and C with B. Yet this will be the inevitable result under the one theory as well as under the other. A mixture of single equivalents of nitrate of baryta and sulphate of potash may be taken as an illustration. Here, as has frequently been shown, if Berthollet's views be correct, at the first moment of mixing, a portion of the baryta combines with sulphuric acid, but that compound being insoluble is instantly put out of the field of action, and the resulting mixture really consists of nitrate of baryta, nitrate of potash, and sulphate of potash, which of course gives rise to a redistribution of the bases and acids, and a further production of insoluble sulphate of baryta, and so on, till the amount of nitrate of baryta remaining is infinitesimally small; while at the same time the whole of the potash must necessarily combine with the whole of the nitric acid. It is scarcely necessary to observe, that this division and precipitation will take place continuously until complete; and that it may be so rapid as to elude our notice.* The fact then that precipitation when it occurs is complete, decides nothing as to the relative merits of the two

* Yet it is easily conceivable that when the affinity for each other of the two substances that produce the insoluble compound is very weak, the action may last some time, and become evident to our senses. Is not this actually the case when sulphate of lime in solution is added to nitrate of strontia, or carbonate of soda to chloride of calcium, or an alkaline carbonate to tartrate of yttria, or oxalate of ammonia to sulphate of magnesia, &c. ?

theories of elective affinity. Yet there is an important difference to be noted. On Bergman's supposition, it can hardly be imagined but that cases will sometimes occur, where A has so strong an affinity for B, or C so powerful an attraction for D, that on mixing AB and CD, no interchange will take place, although AD may be an insoluble body. On Berthollet's supposition, the insoluble compound will always be wholly precipitated whenever by the interchange of acids and bases such a compound can be formed, even though it be against the preponderating direction of the affinities. Now this can be put at once to the test of experience: and what is the testimony of the thousands of double decompositions which chemists are in the habit of meeting with? Graham* says, "It is a general law to which there is no exception, that two soluble salts cannot be mixed without the occurrence of decomposition, if one of the products that may be formed is an insoluble salt." Gmelin†, even when arguing against Berthollet's views, admits the same fact, adding, "the only case which appears to present an exception is that observed by Th. Scherer‡, and this requires further examination." The case, which depends on the insolubility of oxalate of yttria, broke down on careful investigation.

It is then a law, without a single known exception, that if AB, CD, EF, &c., by any interchange of bases and acids, can possibly produce an insoluble substance, that insoluble compound does actually make its appearance. This seems to me almost conclusive evidence that the interchange always takes place originally to a greater or less degree; for I cannot believe, with one chemist of high repute, that "when bodies are brought into intimate contact, all the forces which exist, not only in themselves, but in all their possible compounds, are called into action at the same time," unless indeed it be by these compounds being actually formed.

The following experiments may illustrate more fully the truth of the explanation of complete precipitation which has been given above.

I. Strong solutions of sulphocyanide of potassium and ferric sulphate were mixed. The resulting intensely red liquid was divided into two equal parts. The one portion was largely diluted with water; and to the other portion a little strong alcohol was added, which caused the precipitation of sulphate of potash while ferric sulphocyanide was dissolved. The alcohol was poured off, and diluted with water till of the same volume as the first portion. It was far deeper in colour, indicating evidently that the insolubility of sulphate of potash in alcohol had removed it out of the sphere of action, and had caused a much larger proportion of

* Elements of Chemistry.

† Handbook of Chemistry.

‡ Poggendorff, li. 470.

ferric sulphocyanide to be formed than would otherwise have been produced. Only a small quantity of alcohol was employed, and it was mixed with a large amount of water, in order to obviate as much as possible the objection that the same amount of ferric sulphocyanide might appear darker in alcoholic than in aqueous solution, which is indeed the fact.

II. Another red solution was prepared by mixing sulphocyanide of potassium and ferric sulphate, and it was divided into two equal portions. To one of these hydrochloric acid was added, which of course reduced the colour somewhat. To each was then added an equal portion of neutral phosphate of soda. The acid solution remained red, though paler than before; the neutral solution became colourless, and turbid, from the formation of a flocculent precipitate of ferric phosphate. That the insolubility of this salt in the neutral solution was the cause of the complete combination of the oxide of iron with the phosphoric acid, was further elucidated by adding phosphoric acid to the colourless mixture, which restored a faint red tint to the solution, doubtless because it had set free some of the sulphuric acid, which, redissolving the ferric phosphate, allowed of the formation of a small amount of the red sulphocyanide.

III. A mixture of three parts of ferric citrate, and four of ferrocyanide of potassium was prepared, and divided into two equal parts. To the one there was added a few drops of hydrochloric acid, to the other a few drops of oxalic acid. In the one case, the ferric ferrocyanide, being insoluble in hydrochloric acid, was precipitated, leaving no trace of iron in the solution; in the other case there was a blue solution, but the whole of the iron was not in the condition of ferric ferrocyanide, for the addition of more prussiate of potash caused it to become bluer. That this was due, not to the affinity of the oxalic acid for the ferric oxide, but to that of the citric acid, will be evident from the fact ascertained by the previous experiments on the ferrocyanide, that this result would not have been obtained had the nitrate been employed.

The testimony of volatilisation.—The argument that has been employed in the case of precipitation will apply, *mutatis mutandis*, with equal force in the case of volatilisation. I am not acquainted with any exceptional instance.

The testimony of crystallisation.—It will sometimes happen that certain quantities of AB and CD are mixed in an amount of water which is insufficient to keep in perfect solution AD, should the whole of A combine with the whole of D, although the salt itself is a soluble one. In such a case, if Bergman's view be correct, either no AD will form, however concentrated the solution, or, should double decomposition ensue, it will form to the fullest

extent possible, and may be expected to crystallise out at once with something like the rapidity with which precipitation usually takes place. If, however, Berthollet's theory be a true expression of the fact, a certain amount of AD will always be formed, but it may remain dissolved in the liquid, although if the whole of A had entered into combination with D it must have separated: yet, on concentration, AD will make its appearance; and should this, or anything else, determine the formation of crystals, or should they ensue on the primary mixing, the crystallisable salt is *pro tanto* put out of the field of action, and a redistribution of the acids and bases will take place with further crystallisation, until an equilibrium is obtained. Now the latter of these deductions describes what actually does take place, but there are several circumstances attending crystallisation from a mixture of salts which are not readily explained, and which I have as yet but imperfectly investigated.

The testimony of Malaguti's experiments.—Malaguti* examined the present question by taking two salts, both of which were soluble in water, but only one of which was soluble in alcohol, mixing them in equivalent proportions in water, and then pouring the aqueous solution into a large quantity of alcohol. Notwithstanding an objection recognised by the experimenter, three important results may be arrived at:—1st, that two salts on being mixed resolve themselves into four; 2nd, that this partition takes place in a definite manner; 3rd, that the proportions of the resulting salts are independent of the manner in which the different elements were originally combined.

The testimony of substances acted on by one of the compounds liberated in a mixture of salts.—It is to be expected that if two binary compounds be mixed, the formation of a new compound, though it remain in solution, may often be ascertained by certain chemical powers which it is capable of exerting. Instances of this are not wanting. Thus gold, as every one knows, is not attacked by hydrochloric or nitric acid singly, but is dissolved by a combination of the two; neutral potash salts of course have no action upon it; and yet gold dissolves readily in a mixture of either nitrate of potash and hydrochloric acid, or of chloride of potassium and nitric acid; whence it appears to me the conclusion may be fairly drawn, that in both mixtures the potash relinquishes a portion of the acid with which it was originally combined, or (which is the same thing) that it divides itself between the two.

Such experiments as this have no quantitative value, since the liberated substance immediately enters into a new combination,

* "Exposition de quelques faits relatifs à l'action réciproque des sels solubles," Ann. de Chim. et de Phys. 3, t. xxxvii. p. 198.

which must give rise to a fresh distribution of the different elements, and so on until no more of the active substance can be produced. A mere solvent action of the liberated body would be preferable to an action where positive chemical combination or decomposition takes place; but such cases scarcely exist. Among the actions which appear to answer this requirement most fully, is when a salt insoluble in water is dissolved in an acid, as, for instance, ferric phosphate in hydrochloric acid; yet even here a partial decomposition in all probability ensues. The only instructive numerical results which I have obtained were by mixing a saturated solution of oxalate of lime in hydrochloric acid with various proportions of acetate of potash or soda. The hydrochloric acid combining with the alkali caused a deposition of oxalate of lime, since that salt is not soluble in the acetic acid that was liberated at the same time.

| Acetate of soda series. | | Acetate of potash series. | |
|-------------------------|----------------------------|---------------------------|----------------------------|
| Salt added. | Oxalate of lime deposited. | Salt added. | Oxalate of lime deposited. |
| 3 measures. | 0·075 grm. | 20 meas. | 0·359 grm. |
| 6 measures. | 0·10 grm. | 40 meas. | 0·345 grm. |
| 9 measures. | 0·11 grm. | 80 meas. | 0·410 grm. |
| 12 measures. | 0·13·5 grm. | 120 meas. | 0·445 grm. |
| 18 measures. | 0·14·5 grm. | 160 meas. | 0·503 grm. |
| 30 measures. | 0·11 grm. | 240 meas. | 0·564 grm. |
| 45 measures. | 0·14·5 grm. | | |
| 90 measures. | 0·19 grm. | | |

Notwithstanding certain irregularities in these series of numbers, it is sufficiently evident in both instances that the amount of oxalate deposited increased with the amount of acetate added, though not in direct ratio.

Supposed exceptions and limitations.—With this mass of evidence, and that of a very diversified character, the question arises,—Are we justified in concluding that the principles, which are so general, are *universal* in their application? Are there no exceptions? Is there no limitation?

As to exceptions, in the whole range of my experiments upon this subject, I have never met with a single instance of two substances having so strong an affinity for one another, that they combined to the exclusion of other bodies of like kind and present in the same solution, even if in large excess. Sometimes this rests not on demonstrative, but upon moral evidence, as, for instance,

when sulphocyanide of potassium and dissolved ferric ferrocyanide are mixed, where unquestionably the amount of ferric sulphocyanide produced must be quite inappreciable; yet that some is produced may be safely inferred I think from the fact, that sulphocyanide of potassium does give a red with the ferric acetate, and acetate of potash is capable of decomposing the ferric ferrocyanide to a well-marked extent.

During the controversy that ensued after the publication of Berthollet's treatise, many reactions were brought forward to prove the falsity of his views. Most of these were directed against certain positions of the French philosopher which were certainly untenable, while others were founded on a misapprehension of the question at issue. Those which appear the most formidable against the conclusions arrived at in this paper are, that boracic acid, or carbonic acid, or hydrosulphuric acid, is incapable of decomposing, in the least degree, sulphate of potash or any analogous salt; and that chloride of sodium is not affected at all by iodine. The proof of these statements rests in each instance upon the testimony of blue litmus paper. In the first case, the vegetable colour is not reddened; which is supposed to prove that no sulphuric acid has been liberated; yet if any had been set free there must have been formed at the same instant an equivalent amount of borate, or carbonate, or hydrosulphate of potash, each of which has an alkaline reaction, and would have restored the blue, or rather prevented the litmus from reddening. So in the case of the common salt and iodine (where by the way only one base is concerned), the chlorine, supposing it liberated, would not have bleached the litmus, but would have combined at the moment of its separation with some of the iodine present to form the terchloride of iodine which has a natural reaction. That very little decomposition does take place in these instances I have no doubt, but that there is actually none is not proved.

The action of water requires fuller investigation.

CONCLUSIONS.

The general conclusions arrived at in this paper may be summed up as follows:—

I. Where two or more binary compounds are mixed under such circumstances that all the resulting bodies are free to act and react, each electro-positive element arranges itself in combination with each electro-negative element in certain constant proportions.

II. These proportions are independent of the manner in which the different elements were originally combined.

III. These proportions are not merely the resultant of the various strengths of affinity of the several substances for one another, but are dependent also on the mass of each of the substances in the mixture.

IV. An alteration in the mass of any of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regularly progressive ratio; sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion.

V. This equilibrium of affinities arranges itself in most cases in an inappreciably short space of time, but in certain instances the elements do not attain their final state of combination for hours, or even days.

VI. The phenomena that present themselves where precipitation, volatilisation, crystallisation, and perhaps other actions occur, are of an opposite character, simply because one of the substances is thus removed from the field of action, and the equilibrium that was first established is thus destroyed.

VII. There is consequently a fundamental error in all attempts to determine the relative strength of affinity by precipitation; in all methods of quantitative analysis founded on the colour of a solution in which colourless salts are also present; and in all conclusions as to what compounds exist in a solution drawn from such empirical rules as that "the strongest base combines with the strongest acid."

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V.—*Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre.*

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ALTHOUGH the exact determination of the commercial value of specimens of nitre may, for its importance, be ranked with the valuation of alkalies, manganese-ores, &c., and has, in consequence, occupied the attention of several chemists, it is certain that no method has hitherto been proposed which will enable the analyst to ascertain, with rapidity and precision, the amount of nitrate of potassa contained in any specimen of the saltpetre of commerce.

This assertion appears somewhat startling when it is remembered that several names of no mean authority are connected with the methods hitherto in use ; but it exhibits the conclusion to which the authors have been conducted by a lengthened series of experiments, undertaken in the most perfect faith, not with the intention of shaking the foundations of the different methods of valuing nitre, but rather in order to convince themselves of the soundness of their pretensions to accuracy.

The manner in which this investigation originated is a sufficient proof of the disposition in which the authors commenced their experiments. Samples of nitre having been placed in their hands for very exact valuation, they had recourse to the process commonly

known as that of Pelouze, and were extremely surprised to find, that, with whatever care the experiments were conducted, the results obtained frequently exhibited great variations.

Various modifications of this process having been tried without success, the well-known method of deflagration was resorted to; but here, again, a very great uncertainty attended the experiments, so that an important discrepancy was often apparent in the results of several trials made upon the same sample.

It will be the object of this paper to describe the experiments which have been made upon these two methods, with the intention, firstly, of proving their title to confidence; secondly, of discovering the causes of inaccuracy; and thirdly, of ascertaining whether any modifications could be adopted which would still entitle them to a position among trustworthy analytical processes.

Before entering upon the experimental details, it may be deemed necessary to take a brief historical survey of the methods which have been employed at different times to ascertain the commercial value of saltpetre. These may be divided, with respect to the principles upon which they are founded, into mechanical and chemical methods.

The Swedish process of Swartz, which probably originated the term "refraction of saltpetre," consisted in an examination of the fracture of a cake of the fused salt, which could not certainly lead to any accurate numerical results.

A far more important mechanical method is that of Riffault, which appears to have been proposed in 1789, and has since been very generally used in the refineries of France. It consists in washing a weighed quantity of nitre with a saturated solution of the pure salt, and in determining the amount of the residue. The errors to which such a process must be liable are too obvious to need detailed consideration: they are chiefly attributable to the presence of chloride of sodium in the samples examined, and to the variations of temperature, which must depend upon the quantities of chlorides present; other objections of great weight at once suggest themselves to every practical chemist.

The Austrian method, proposed by Husz, consists in an exact determination of the temperature at which an aqueous solution of the sample begins to deposit crystals; but this is evidently liable to disturbance from the presence of chloride of sodium, and requires, moreover, greater delicacy of observation than should be necessary for a process to be carried on in a general chemical laboratory.

The authors have not considered it necessary to subject these

mechanical methods to any lengthened examination, believing that the opinion of chemists upon their inaccuracy is unanimous, and that their general adoption has been owing, not to their intrinsic merit, but to the want of more trustworthy processes.

There are only two well-known methods of valuing nitre, in general use, which are based upon chemical principles. The older method, usually known as that of Gay-Lussac, consists in converting the nitrate into carbonate of potassa, by deflagration with charcoal, the amount of the alkaline carbonate being afterwards determined by the alkalimeter.

The later process was introduced by Gossart,* and consists in ascertaining the amount of protoxide of iron converted into sesquioxide by a given weight of the sample of nitre. As originally proposed, a solution of protosulphate of iron, of known strength, was added to the acidified solution of nitre, until the presence of an excess of the protosalt could be discovered by ferriecyanide of potassium, but experience had manifested the inaccuracy of this proceeding. Pelouze† modified it by dissolving a known weight of iron, converting a portion into sesquioxide by a given weight of the sample of nitre, and afterwards determining the unoxidised portion, by the method of Margueritte, with a standard solution of permanganate of potassa.

The following table contains the results of several trials of this method, conducted exactly according to the directions given by its author:—

TABLE I.

| Exp. | Nitre. | Iron. | Iron unoxidised. | Nitre found. | Nitre per cent. |
|------|--------|--------------------------------|------------------|--------------|-----------------|
| 1†. | 18.53 | 31.00 | 0.85 | 18.12 | 99.40 |
| 2. | 18.50 | Gave a result somewhat higher. | | | |
| 3. | 20.10 | 30.00 | 0.75 | 17.58 | 87.46 |
| 4. | 20.16 | 30.00 | 0.37 | 17.81 | 88.33 |
| 5. | 20.05 | 30.00 | 0.41 | 17.78 | 88.67 |
| 6. | 20.18 | 31.00 | 0.30 | 18.45 | 91.42 |
| 7. | 20.26 | 33.50 | 0.30 | 19.95 | 98.48 |
| 8. | 17.83 | 32.80 | trace | 19.71 | 110.55 |
| 9. | 17.80 | 33.26 | 1.50 | 19.09 | 107.20 |
| 10. | 17.64 | 32.46 | 0.30 | 19.33 | 109.50 |
| 11. | 14.56 | 30.40 | 3.10 | 16.41 | 112.70 |

* Compt. rend. January 1847.

† Ann. Ch. Phys. June 1847.

‡ Experiments 1 to 11 inclusive were made with the same sample of *crude* nitre.

TABLE I. (continued.)

| Exp. | Nitre. | Iron. | Iron unoxidised. | Nitre found. | Nitre per cent. |
|------|--------|-------|---------------------|-----------------|--------------------|
| 12*. | 15.00 | 35.12 | 10.25 | 15.12 | 100.80 |
| 13. | 10.00 | 30.31 | 12.51 | 10.80 | 108.00 |
| 14. | 18.00 | 32.64 | 3.08 | 17.97 | 99.83 |
| 15. | 10.00 | 28.06 | 11.14 | 10.28 | 102.80 |
| 16. | 19.00 | 33.57 | 1.95 | 19.22 | 101.05 |
| 17. | 19.00 | 32.42 | 0.31 | 19.52 | 102.73 |
| 18. | 19.00 | 32.83 | 1.04 | 19.32 | 101.68 |
| 19. | 17.60 | 30.53 | 0.31 | 18.37 | 104.37 |

In most of these experiments, the iron was dissolved in concentrated hydrochloric acid, in a flask furnished with a cork and glass tube drawn out to a fine point. As soon as the metal had disappeared, the cork was withdrawn, the nitre washed in as quickly as possible, the cork replaced, and the solution boiled until the brown colour due to the nitric oxide had disappeared: it was then rinsed into a large flask, diluted with about 40 oz. of water, and the amount of iron left unoxidised was determined by means of a dilute solution of permanganate of potassa.

In Experiment 9, the nitre was dissolved in water and poured into the boiling solution while hydrogen was being evolved.

In Experiment 10, the solution of nitre was poured down a funnel tube, the extremity of which dipped into the acid solution of iron, a column of this solution having been made to ascend in the tube by a momentary closing of the egress tube, so that no air whatever was introduced.

In Experiment 11, the nitre was placed in a small bottle; which was suspended in the flask by a horsehair, and was only let down when the iron was completely dissolved; a layer of carbonate of soda was placed over the nitre, to prevent any premature contact with drops of the acid liquid.

In Experiment 12, the solution was boiled for half an hour after the introduction of the nitre; in Experiment 16, the boiling was continued for six minutes only; in Experiment 17, for twenty minutes; and in Experiment 18, the solution was boiled nearly to dryness.

An examination of this table leads to some curious inferences respecting the general working of the process.

The first experiment, in which the quantities employed were

* Experiments 12 to 19 were made with perfectly pure nitre.

almost exactly those recommended by Pelouze—viz. 2 grms. (30·9 grs.) of iron and 1·2 grm. (18·5 grs.) of nitre—furnished a result which might have been accepted with confidence had the sample of nitre been supposed nearly pure.

In the third, fourth, and fifth experiments, where the quantity of iron was diminished, and that of the nitre increased, the amount of nitre indicated by the oxidised iron fell very considerably; and between these three experiments, the quantities employed being nearly the same, no great discrepancy is observed.

When, however, as in the sixth and seventh experiments, the quantity of the iron is increased, though that of the nitre remains the same, a very considerably higher result is obtained.

In seeking for the cause of these variations, the attention of the authors was first directed to that adverted to by Pelouze—viz. the access of air to the solution containing the brown compound of the protosalt of iron with nitric oxide, the tendency of this solution to absorb oxygen being well known. The additional precautions taken to exclude air in the ninth and following experiments, had no effect in diminishing the error, which was, indeed, greater in these experiments than in those where no great precautions were adopted. The sixteenth and following experiments prove that the duration of the ebullition is also without effect upon the result.

In conducting these experiments, it was found difficult to hit the exact point at which the addition of the solution of permanganate of potassa should be discontinued; and since it was possible that this might give rise, in some degree, to the discrepancy in the results, a number of experiments were made, in which moderately diluted sulphuric acid was substituted for the hydrochloric, when no such difficulty was experienced, the colour of the sesquisulphate of iron being far lighter than that of the sesquichloride.

TABLE II.

| Exp. | Nitre. | Iron. | Iron unoxidised. | Nitre found. | Nitre per cent. |
|------|--------|-------|---------------------|-----------------|--------------------|
| 1. | 10·00 | 22·43 | 5·89 | 10·05 | 100·50 |
| 2. | 10·00 | 20·00 | 3·46 | 10·05 | 100·50 |
| 3. | 10·00 | 31·94 | 16·04 | 9·67 | 96·70 |
| 4. | 6·00 | 21·43 | 10·91 | 6·39 | 106·50 |
| 5. | 6·00 | 20·20 | 8·91 | 6·86 | 114·33 |
| 6. | 6·00 | 20·05 | 9·51 | 6·40 | 106·66 |
| 7. | 6·00 | 21·63 | 11·71 | 6·03 | 100·50 |
| 8. | 10·00 | 32·14 | 15·91 | 9·87 | 98·70 |

TABLE II. (continued.)

| Exp. | Nitre. | Iron. | Iron unoxidised. | Nitre found. | Nitre per cent. |
|------|--------|-------|---------------------|-----------------|--------------------|
| 9. | 10·00 | 21·35 | 3·82 | 10·60 | 106·00 |
| 10. | 10·00 | 30·18 | 13·73 | 10·00 | 100·00 |
| 11. | 10·00 | 21·55 | 3·65 | 10·88 | 108·80 |
| 12. | 15·00 | 32·20 | 6·22 | 15·79 | 105·26 |
| 13. | 15·00 | 32·95 | 4·94 | 17·03 | 113·53 |
| 14. | 18·00 | 30·49 | 0·51 | 18·53 | 102·94 |
| 15. | 18·00 | 31·02 | 1·80 | 17·76 | 98·66 |
| 16. | 18·00 | 31·13 | 1·69 | 17·90 | 99·44 |
| 17. | 18·00 | 31·27 | 1·63 | 18·02 | 100·11 |
| 18. | 18·30 | 31·49 | 1·30 | 18·35 | 100·27 |
| 19. | 10·00 | 30·80 | 13·80 | 10·30 | 103·00 |
| 20. | 18·30 | 31·16 | 2·10 | 17·77 | 97·10 |
| 21. | 18·30 | 30·36 | 0·56 | 18·11 | 98·96 |

In these experiments some difficulty occasionally arose from the separation of an insoluble sulphate of sesquioxide of iron, which was only redissolved with considerable difficulty, and much interfered with the ebullition. In Experiments 5 and 13, the boiling was continued for a short time only, and the solution had still a brown tinge.

In Experiments 15, 16, and 17, the solution was boiled as long as possible; while in Experiment 18 it was boiled only for a short time.

It is apparent from this table, that, although the results obtained with sulphuric acid are generally more concordant than those obtained with hydrochloric acid, there is yet too great a variation observed in the results of several experiments, conducted as nearly as possible under the same conditions, to allow of any implicit confidence.

The results occasionally exhibited, both in this and in the preceding table, are sufficient to show that there is no want of correctness in the broad principle of the method, since several experiments in succession may furnish numbers agreeing very closely with each other. The cause of the remarkable variations occasionally observed must rather be sought for in some circumstance not directly connected with the theory of the operation.

Attention was therefore next directed to the discovery of some modification of the method which should so far diminish the frequency of the variations as to render it capable of application in commercial analysis.

Previously, however, to advancing in this branch of the inquiry, it was considered necessary to institute a few experiments in confirmation of the view generally taken respecting the action of nitric oxide upon the protosalts of iron.

5 grs. of iron were dissolved in hydrochloric acid, in a flask through which a stream of carbonic acid was passed in order to exclude air: when the iron was entirely dissolved, the flask was connected with an apparatus from which binoxide of nitrogen (prepared by the action of dilute nitric acid upon copper, and transmitted through water) was passed to complete saturation; the solution was then boiled while a stream of carbonic acid was passed through it, until all the binoxide of nitrogen was expelled. The solution of permanganate of potassa indicated 4·962 grs. of iron, showing that nitric oxide is without effect if air be excluded.

Three experiments with larger quantities of iron confirmed this result:—

| Exp. | Iron employed. | Recovered. |
|------|----------------|------------|
| 1. | 13·88 | 13·79 |
| 2. | 15·08 | 15·00 |
| 3. | 14·99 | 14·88 |

3 grs. of iron were dissolved in a similar manner, and, the solution having been saturated with nitric oxide, the cork and tubes were very rapidly withdrawn, replaced by a cork with a capillary tube, and the experiment terminated as usual; the permanganate of potassa then indicated only 1·602 grs. of unoxidised iron, nearly one-half of the protoxide having been converted into sesquioxide by the air admitted when the cork was changed.

Some experiments were then tried in which the solution, after saturation, was boiled only for five minutes in the stream of carbonic acid, when it was found that although the brown colour of the solution had changed to a light yellow, there must still have been a little nitric oxide left in the liquid when it was brought in contact with the air, since a considerable amount of iron had been peroxidised.

| Exp. | Iron employed. | Iron recovered. |
|------|----------------|-----------------|
| 1. | 14·96 | 13·75 |
| 2. | 14·44 | 14·02 |
| 3. | 13·35 | 13·22 |
| 4. | 11·49 | 11·40 |

When the solution of protochloride of iron was saturated with

nitric oxide in a flask filled with carbonic acid, and the iron determined without boiling, an excess of the solution of permanganate of potassa was consumed.

| Exp. | Iron employed. | Iron recovered (apparently). |
|------|----------------|---------------------------------|
| 1. | 12·81 | 16·00 |
| 2. | 12·85 | 14·40 |
| 3. | 12·12 | 16·25 |

This result was explained when some nitric oxide was passed into water, in a flask filled with carbonic acid, and permanganate of potassa was afterwards added, when a rapid deoxidation took place, but only upon the surface.

The action of nitric oxide upon the acid solution of protosulphate of iron was then examined.

11·68 grs. of iron were dissolved in sulphuric acid, the solution saturated with nitric oxide, in a flask filled with carbonic acid, and the nitric oxide subsequently expelled by boiling the solution, when the stream of carbonic acid was rapidly passed; the permanganate of potassa then indicated 11·63 grs. of iron, proving that, if air be excluded, nitric oxide is without effect upon the solution.

Four experiments conducted in a similar manner, except that the stream of carbonic acid was not continued while the nitric oxide was being expelled, showed how slight an access of air can modify the result.

| Exp. | Iron employed. | Iron recovered. |
|------|----------------|-----------------|
| 1. | 13·76 | 13·47 |
| 2. | 12·14 | 11·93 |
| 3. | 11·04 | 10·45 |
| 4. | 12·14 | 11·70 |

In the following experiments, the solution was treated with binoxide of nitrogen in a flask filled with carbonic acid, the excess of the binoxide afterwards displaced by that gas, and the iron determined without boiling the solution.

| Exp. | Iron employed. | Iron recovered. |
|------|----------------|-----------------|
| 1. | 11·05 | 11·02 |
| 2. | 11·93 | 11·91 |
| 3. | 13·02 | 13·06 |
| 4. | 12·03 | 12·04 |
| 5. | 12·32 | 12·24 |

The difference cannot fail to be remarked between the results in these cases, and in the corresponding experiments with the hydrochloric solution,—a difference which may perhaps be explained by the circumstance that a more stable compound is formed by nitric oxide with the protosulphate than with the protochloride of iron, and therefore that, in the case of the sulphuric solution, the residual binoxide of nitrogen does not so readily undergo partial oxidation at the expense of the air, and thus become capable of reducing the permanganate. Some confirmation is afforded to this view by the circumstance that the expulsion of the nitric oxide from the sulphuric solution is far more gradual and difficult than when hydrochloric acid has been employed.

From these experiments it is quite evident that the binoxide of nitrogen is without effect upon the acid solutions of the protosalts of iron, if air be entirely excluded, but that unless the most rigid precautions are taken to ensure this, an oxidation of a part of the protoxide of iron is inevitable.

It then became necessary to endeavour to modify the process in such a manner as to preclude the possibility of an error from this cause.

The iron was dissolved in hydrochloric acid, in a flask filled with carbonic acid gas, and the nitre, having been suspended in a small tube, was let down into the solution when all the air had been expelled; in this case far too little nitre was obtained. Imagining that the deficiency might be due to the action of the vapour of hydrochloric acid upon the nitre, the latter was covered in the tube with a layer of bicarbonate of soda, but still a great deficiency was observed. In order to avoid any possibility of error from the rapid evolution of carbonic acid when the tube was allowed to fall into the liquid, a layer of borax was substituted for the bicarbonate, but only 93 parts for 100 of nitre were obtained.

In order to ascertain how far the loss might be due to the expulsion of nitric acid, as such, when the nitre came suddenly in contact with the boiling liquid, two experiments were made, in an apparatus filled with carbonic acid, the nitre being introduced only when the solution had quite cooled. The first gave 89, the second 94 per cent. of nitre in the pure salt.

A few of the experiments tried with every precaution to exclude air gave very accurate results, but the circumstances regulating these appeared to be so far beyond control, that it was impossible to obtain similar results from three or four experiments in succession, conducted with apparently equal care. The experiments were

varied by employing sulphuric instead of hydrochloric acid, but without any beneficial result.

With a view to ascertain how far the errors might be connected with the imperfect deoxidation of the nitric acid by the protosalt of iron, the following experiments were undertaken, in which the evolved gas was collected and examined.

22·93 grs. of iron were dissolved in dilute sulphuric acid (sp. gr. 1·3), and, as soon as all the air had been expelled, 14 grs. of nitre, contained in a small tube, were dropped into the liquid, the gas being collected over mercury: after the ebullition had been continued until the brown colour of the liquid had disappeared, the volume of gas was 11 cub. in.

2 cub. in. of this gas, exposed to the action of hydrate of potassa, did not diminish in volume.

2 cub. in., treated with solution of protosulphate of iron, left only 0·03 cub. in. unabsorbed; it therefore consists of nearly pure nitric oxide, the small unabsorbed portion being due probably to the residual air.

Theoretically, the 14 grs. of nitre should have yielded 12·98 cub. in. of nitric oxide.

The amount of nitre inferred from the determination of the unoxidised iron was only 86 per cent., while the 11 cub. in. of binoxide of nitrogen would represent 84 per cent., which is sufficient to show that the oxidation of the iron is attended with a *corresponding* evolution of that gas.

In a second experiment, the nitre was covered with a layer of borax, to prevent any loss of nitric acid from the spirting of the acid liquid into the bottle.

| | | | | | | |
|-------------------|---|---|---|---|-------|----------|
| Iron employed | . | . | . | . | 47·3 | grs. |
| Nitre „ | . | . | . | . | 15·3 | „ |
| Total vol. of gas | . | . | . | . | 12·75 | cub. in. |

which was proved, as before, to be pure nitric oxide.

Theoretically, 14·9 cub. in. of gas should have been obtained.

The amount of nitre corresponding to the iron oxidised was 90·6 per cent., while the 12·75 cub. in. of gas would represent 89·15 per cent. of nitre.

This affords a still closer confirmation of the general opinion respecting the action of nitre upon the acid solutions of protosalts of iron.

Two additional experiments exhibited the marked deficiency in the nitric oxide evolved.

| Exp. | Iron. | Nitre. | Nitric oxide. | Nitre calculated from the nitric oxide. | |
|------|-------|--------|----------------|--|-------------|
| 1. | 20·81 | 12·17 | 10·89 cub. in. | 11·74 | 96·46 p. c. |
| 2. | 42·07 | 17·54 | 13·17 „ | 14·09 | 80·33 „ |

The next question for consideration was, what became of the nitric acid not represented by the binoxide of nitrogen evolved? With reference to this point, an experiment was made in such a manner that the steam evolved while the nitre remained suspended in the flask could be passed into a solution of blue litmus. The latter was not perceptibly reddened, showing that no nitric acid was carried off in consequence of the accidental contact with drops of sulphuric acid before the salt was allowed to fall into the liquid.

| | | | | | |
|---------------|---|---|---|-------|----------|
| Iron employed | . | . | . | 29·89 | grs. |
| Nitre „ | . | . | . | 17·80 | „ |
| Nitric oxide | . | . | . | 14·65 | cub. in. |

which correspond to only 15·68 grs. of nitre, or 88·09 per cent.

In the following experiment, the evolved gas was passed through a solution of pure carbonate of soda, which was afterwards evaporated to dryness. A portion of the residue, when treated with dilute sulphuric acid, evolved red fumes of nitrous acid: after boiling the liquid till no more red fumes were evolved, abundance of nitric acid was detected by the tests with indigo and sulphate of iron, showing that nitrous (and perhaps nitric) acid had escaped deoxidation.

| | | | | | |
|--|---|---|---|-------|----------|
| Iron employed | . | . | . | 33·95 | grs. |
| Nitre „ | . | . | . | 19·66 | „ |
| Nitric oxide (after removing the carbonic acid) | . | . | . | 13·52 | cub. in. |

corresponding to only 73·58 per cent. of nitre.

To prove that no error was caused by the method of suspending the nitre in this experiment, another was performed in the same manner, except that the tube containing the nitre was allowed to remain suspended above the surface of the boiling acid liquid, as usual, and not allowed to drop down: in this case no trace of nitrous or nitric acid was found in the solution of carbonate of soda.

In the next experiment, the tube containing the nitre was not suspended by a horsehair, but merely lodged on a cork shelf in the neck of the flask, so that it could be allowed to descend into the liquid by merely turning the flask,—thus preventing any error

which might be caused by the accidental admission of air while loosening the cork to disengage the horsehair.

45 grs. of iron and 20 of nitre were employed, and the gas was passed, as before, through a solution of carbonate of soda, which was afterwards found to contain little nitrous acid, but a considerable quantity of nitric acid. The solution remaining in the boiling-flask after the experiment was decomposed with carbonate of soda (previously tested for nitric acid) filtered from the iron precipitate, evaporated to dryness, treated with an excess of dilute sulphuric acid, which did not evolve any fumes of nitrous acid, afterwards mixed with a large quantity of concentrated sulphuric acid, and distilled. When a part of the liquid had distilled over, it was tested with solution of indigo, which indicated scarcely a trace of nitric acid, although this could be very readily detected in the contents of the retort. Moreover, no nitric acid could be found in the succeeding portions of the distillate, although the distillation was pushed to the utmost.

This observation possesses some importance in an analytical point of view, explaining, as it does, the inaccuracy (generally acknowledged) of the method of determining nitric acid in the nitrates by distilling with sulphuric acid, and proving the necessity for caution in testing for nitric acid by this method. Several experiments afforded full confirmation of the fact that nitric acid, and occasionally nitrous acid, could be found in the vapours evolved during the action of the nitre upon an acid solution containing a large excess of protosulphate of iron, and that the solution in the flask often contained a considerable quantity of undecomposed nitric acid.

It naturally excited great surprise that nitric acid should be capable of existing, though in relatively small quantity, in a solution of protosulphate of iron which contained a large excess of sulphuric acid, and had been boiled for a considerable time. Numerous experiments, however, made with the greatest care and with varying proportions, have perfectly convinced the authors of the fact. Judging from the experiment above mentioned, where the nitric acid could not be recovered by distillation, it would seem probable that this acid may be supposed to have remained in the solution in the form of undecomposed nitrate of potassa,—a supposition which is assuredly less preposterous than that it should exist in the free state.

It still remained to be proved whether the action of a hydrochloric solution was similar to that in which sulphuric acid was used.

The nitre was suspended, as usual, in a small tube, and covered with a layer of carbonate of soda; the evolved gas was passed into water excluded from air. This was found, after the experiment, to contain a very slight trace of nitric acid.

| | | | | |
|-----------------|---|---|-------|------|
| Iron employed | . | . | 35.67 | grs. |
| Nitre „ | . | . | 15.00 | „ |
| Iron unoxidised | . | . | 11.23 | „ |

indicating 99.06 per cent. of nitre.

The evolved gas consisted only of nitric oxide mixed with a little carbonic acid from the carbonate of soda.

No appreciable quantity of chloride of iron was found in the water through which the gas had been passed.

Another experiment was performed in a similar manner, the evolved gas being conducted through a solution of carbonate of soda, which was found to contain a trace of nitric acid after the experiment.

No nitric acid could be detected in the iron solution.

In a third experiment, with similar proportions, the gas was first passed into a small flask containing water (to absorb the hydrochloric acid), and then into a flask containing a considerable quantity of moistened carbonate of soda.*

The iron solution was decomposed by carbonate of soda, and carefully tested for nitric acid, but without result.

An experiment was then made in which the tube containing the nitre (covered with carbonate of soda) was allowed to slip down into the solution without loosening the cork.

In this case, also, abundance of nitric acid was found in the condensing flask.

| | | | | |
|-----------------|---|---|-------|------|
| Iron employed | . | . | 34.52 | grs. |
| Nitre „ | . | . | 15.00 | „ |
| Iron unoxidised | . | . | 10.61 | „ |

corresponding to 96.8 per cent.

To prove that the nitric acid was not accidentally carried over before the nitre was brought in contact with the iron solution, the last experiment was repeated, but without allowing the nitre to drop into the flask: in this case, although the ebullition was continued for an unusual period, no trace of nitric acid could be detected in the condensing flask.

* It is worthy of remark that in this case the water in the condensing-flask contained a very appreciable amount of iron. A small amount of nitric acid was also found in this flask, but a far larger quantity in that containing the carbonate of soda: no nitrous acid was detected.

In one experiment, a layer of quicklime was placed over the nitre, to prevent any loss of nitric acid due to the sudden evolution of carbonic acid from the carbonate of soda; but in this case only 95·6 per cent. of nitre was obtained, and a considerable quantity of nitric acid was found in the condensing-flask.

The most important conclusions which can be drawn from the experiments above detailed may be stated as follows:—

1. That the reaction upon which the method in question is founded is perfectly correct, and therefore it frequently happens that most accurate results are furnished by it; but

2. That these results are extremely liable to certain disturbing causes, which are so far beyond the control of the operator as to deprive the method of that certainty so essential to any process in use for commercial analysis.

3. That a very important source of error, in the ordinary mode of proceeding, is the absorption of oxygen from the air; and although the oxidation, through the intervention of the nitric oxide with which the flask is filled, may be prevented by simple arrangements, it is very difficult, especially when sulphuric acid is employed, to ensure the complete expulsion of the nitric oxide from the iron solution; and when the latter, containing still a little of this gas, is brought in contact, at a high temperature, with the air, oxidation immediately ensues, thus causing an apparent increase in the amount of nitre obtained. This source of error was adverted to by Pelouze in his original memoir.

4. That a variable quantity of nitric (and sometimes of nitrous) acid escapes unreduced, when nitrate of potassa is introduced into boiling acid solutions of protochloride or protosulphate of iron, even in large excess.

5. That when nitrate of potassa is introduced into a boiling solution of protosulphate of iron, containing a large excess of sulphuric acid, an appreciable quantity of nitric acid may remain in the solution, even after prolonged ebullition.

The authors next examined the method of Gay-Lussac.

Since, apart from other considerations, the accuracy of this process depends upon the degree of precision with which neutralisation is effected by means of an acid of known strength, it became necessary to institute some experiments for the purpose of determining the essential conditions for attaining this object.

The measure employed for the acid was a tube *burette*, of the form now generally in use, having a fine opening for delivering the

acid. This instrument was capable of containing 1000 grains of water, and was divided into 200 equal parts.

The different specimens of acid employed were so far diluted that a little less than 1000 grain-measures were required to neutralise the amount of carbonate of potassa corresponding to 20 grains of nitre. An acid of this description contains from 8· to 8·5 grains of SO_3 in 1000 grain-measures. The strength of the acid having been approximately ascertained by the neutralisation of a known weight of carbonate of soda, was finally determined with the greatest possible accuracy by precipitation as sulphate of baryta.

An aqueous infusion of litmus, free from alkali, was employed to colour the solution under examination, the same quantity being used in every case, so as to impart a rather deep blue colour to the liquid.

It was found, by several preliminary experiments, that the transition of the colour of the litmus was difficult to appreciate exactly, until the liberated carbonic acid had been expelled, on account of the wine-red tint which the latter imparted to the liquid. Experiments with pure carbonate of soda showed that no difference in the results was obtained, whether the carbonic acid was removed by exposure *in vacuo* or by ebullition. The most convenient method of proceeding is to add to the coloured alkaline liquid, contained in a flask, a sufficient quantity of acid to produce the wine-red tint; to heat the mixture to ebullition, adding a few drops of acid from time to time, until the peculiar onion-skin-red colour, imparted by the stronger acids to litmus, is obtained. The accurate appreciation of the colour is much facilitated by using, as a standard of comparison, a similar quantity of coloured water, to which a few drops of sulphuric acid have been added.

In the latter part of the present series of experiments, it was customary to continue the addition of the acid, drop by drop, to the solution, which was boiled after each addition, until it failed to produce in the liquid a cloud of a lighter colour. The observations were made by holding the flasks at a little distance over a sheet of white paper.

The lamp-black employed in the experiments left merely an inconsiderable amount of residue upon incineration. It was thoroughly ignited in a closed crucible before use. The chloride of sodium was perfectly pure, and carefully dried.

A number of experiments were first made with the proportions generally recommended in chemical works; namely, 1 part of lamp-black, 4 of nitre, and 24 of salt: 20 grains of nitre were

employed for most of the experiments. This was mixed with the lamp-black in a platinum crucible, with the aid of a glass rod. The chloride of sodium was then added, and a very intimate mixture effected in the same manner. The crucible was then covered and cautiously heated, so that deflagration might take place with moderate violence. It was afterwards heated to redness for two or three minutes. On cooling, the mass was thrown into a beaker, treated with hot water, the residual carbon filtered off and completely washed, and the alkalinity determined according to the manner above described.

TABLE III.

| Exp. | Nitre found. | Nitre per cent. |
|------|--------------|-----------------|
| 1. | 19.84 | 99.20 |
| 2. | 19.95 | 99.75 |
| 3. | 19.95 | 99.75 |
| 4. | 19.74 | 98.70 |
| 5*. | 18.74 | 93.70 |
| 6*. | 18.89 | 94.45 |
| 7*. | 19.34 | 96.70 |
| 8†. | 15.77 | 93.80 |
| 9‡. | 17.13 | 85.65 |
| 10. | 19.86 | 99.29 |
| 11. | 19.99 | 99.99 |
| 12. | 19.09 | 95.45 |
| 13. | 19.59 | 97.95 |
| 14. | 19.59 | 97.95 |
| 15. | 19.88 | 99.40 |
| 16†. | 17.66 | 88.30 |
| 17†. | 17.96 | 89.80 |
| 18. | 19.79 | 98.95 |

In No. 7 the ingredients were very intimately mixed in a mortar, with a view of ascertaining whether the deficiency in former experiments might have arisen from imperfect mixture.

No. 11 was not heated after the deflagration had ceased.

Nos. 10, 12, 13, and 14 were heated to full redness for five minutes after deflagration had ceased.

It will be seen, from the results contained in the preceding table, that considerable uncertainty attends this method of proceeding;

* Nos. 5, 6, and 7 were portions of the same commercial sample of nitre, known to contain not less than 98 per cent.

† No. 8 consisted of a mixture of 95 parts of pure nitre with 3 parts of chloride of sodium and 2 parts of sulphate of potassa, made to imitate a specimen of commercial nitre. The quantity employed was 16.83 grains.

‡ Nos. 9, 16, and 17 consisted of a similar mixture, containing 90 per cent. of pure nitre.

for, although several of the numbers approach very nearly to those required by theory, others exhibit a very considerable deficiency, without any essential difference in the manner of conducting the experiments in each case.

Experiments were next made to determine whether the method of mixing the ingredients, or the degree and duration of the heat applied, exerted any important influence over the results. Some determinations, in which the materials were intimately mixed in a mortar and heated, in some cases merely with a spirit-lamp, in others to complete fusion of the mass, yielded results exhibiting similar discrepancies to those formerly observed.

After it had been shown, by experiments conducted in such a manner that the volatile products could be collected and examined, that no volatilisation of potassium took place during the deflagration, and that no appreciable amount of alkali remained adhering to the residual carbon, some determinations were made with a view of ascertaining whether the deoxidation of the nitre, in the presence of an excess of carbon, was in all cases complete.

60 grains of pure nitre, 15 of lamp-black, and 360 of chloride of sodium, were deflagrated at a fair red heat. The mass was extracted with water in the usual manner, and the residual charcoal weighed: it amounted to 6.1 grains. The aqueous solution was concentrated by evaporation, and mixed with strong sulphuric acid, when it evolved a powerful odour of chlorine, and exerted a decided bleaching action upon indigo, indicating the presence of nitric acid.

Another similar experiment, in which the usual quantities of the ingredients were employed, gave only 91.95 per cent. of nitre. The presence of unaltered nitric acid in the solution of the deflagrated mass was shown also in this case. A repetition of the experiment gave a similar result.

In two other determinations, the amount of alkali was estimated by the use of hydrochloric acid of known strength, in place of sulphuric acid; the neutralised solutions being subsequently evaporated, and the residues again ignited with an additional quantity of lamp-black, in order to determine quantitatively the nitre left unchanged.

1. 20 grains of nitre were employed; the amount of alkali produced in the first deflagration corresponded only to 19.34 grs., or 96.70 per cent. of nitre. The second deflagration of the neutralised residue gave 0.53 grs. of nitre, or 2.65 per cent.; giving a total of 99.35 per cent.

2. 20 grains of nitre yielded by the first deflagration 19.46 grs.,

or 97·3 per cent. ; by the second, 0·59 of unaltered nitre : making in all 100·25 per cent.

Hence it will appear that, allowing for the unavoidable errors in these processes, the amount of nitre left unchanged after the first deflagration just supplied the deficiency.

Table IV. contains the results of some experiments made with the modifications above alluded to.

TABLE IV.

| Exp. | Nitre found. | Nitre per cent. |
|------|--------------|-----------------|
| 1. | 19·84 | 99·20 |
| 2*. | 18·39 | 91·95 |
| 3†. | 17·21 | 86·05 |
| 4‡. | 18·43 | 92·18 |
| 5‡. | 19·64 | 98·20 |
| 6‡. | 19·09 | 95·45 |
| 7. | 19·59 | 97·95 |

In the preceding table, only those experiments are quoted which exhibited any remarkable deficiency. It must, in fairness, be stated that in some other experiments made under similar circumstances very satisfactory numbers were obtained, although no reason for the difference could be traced in the method of proceeding.

It naturally suggested itself that some alteration in the proportions of the ingredients might *ensure* a more accurate result ; and with this view the experiments given in Table V. were undertaken.

TABLE V.
(Nitre employed, 20 grs.)

| Exp. | Lamp-black. | Salt. | Nitre found. | Nitre per cent. |
|------|-------------|-------|--------------|-----------------|
| 1§. | 8·0 | 120 | 19·10 | 95·50 |
| 2. | 10·0 | 120 | 20·10 | 100·50 |
| 3. | 10·0 | 120 | 19·84 | 99·20 |
| 4 . | 3·0 | 120 | 18·59 | 92·95 |
| 5 . | 3·5 | 120 | 19·72 | 98·60 |
| 6. | 3·5 | 120 | 19·59 | 97·95 |
| 7¶. | 5·0 | 80 | 17·86 | 89·30 |
| 8**. | 10·0 | 120 | 18·89 | 94·45 |

* No. 2 was heated in a muffle to complete fusion, after deflagration.

† Nos. 3 and 4 were made with an artificial mixture containing 95 per cent. of nitre.

‡ In Nos. 5 and 6 the residual carbon was weighed, and subsequently incinerated. In No. 5, 1·6 grs. of charcoal was left unconsumed, and yielded 0·11 of ash. In No. 6, 1·2 grs. of charcoal was left, and furnished 0·076 of ash.

§ In No. 1, 20·1 grs. of nitre were employed.

|| In Nos. 4 and 5, nitric acid was detected after the deflagration, although some carbon was left unconsumed.

¶ No. 7 was made with a mixture containing 92 per cent. of nitre.

** No. 8 was projected by degrees into the crucible.

The numbers above quoted show that neither the increase nor the diminution of the amount of lamp-black was attended with any beneficial result. Indeed, the alterations in the proportions appeared to increase the chances of error, satisfactory results being much less frequently obtained.

On examining the various specimens of lamp-black employed in all the experiments alluded to, they were found to contain a very appreciable amount of sulphur. Since it was deemed possible that the presence of this impurity might exert some influence upon the results obtained, it was determined to substitute, for the lamp-black, charcoal obtained by the complete calcination of washed starch.

Table VI. contains results of some of the determinations made with this variety of charcoal.

TABLE VI.
(Nitric employed, 20 grs.)

| Exp. | Charcoal. | Salt. | Nitric found. | Nitric per cent. |
|------|-----------|-------|---------------|------------------|
| 1. | 10 | 80 | 21.60 | 108.00 |
| 2. | 10 | 80 | 20.35 | 101.75 |
| 3. | 10 | 80 | 21.10 | 105.50 |
| 4. | 10 | 120 | 21.10 | 105.50 |
| 5. | 10 | 80 | 21.05 | 105.25 |
| 6*. | 10 | 80 | 20.60 | 103.00 |
| 7. | 20 | 80 | 21.60 | 108.00 |
| 8. | 20 | 80 | 21.35 | 106.75 |
| 9. | 20 | 80 | 21.85 | 109.25 |
| 10. | 30 | 80 | 20.22 | 101.10 |
| 11. | 20 | 80 | 20.52 | 102.59 † |

These results naturally excited surprise, as in every case the amount of carbonate of potassa indicated by the standard acid considerably exceeded that which corresponded to the amount of nitric present. They served, however, to recall to mind the circumstance that an excess had occasionally been obtained in the former experiments, in which lamp-black was employed, but on which little stress had been laid, since they were comparatively so seldom met with as to be attributed to some accidental circumstance.

* In No. 6 the quantities were doubled, 40 grs. of nitric being employed, to see whether the error was much diminished.

† Two experiments were made, in which wood-charcoal was substituted for charcoal from starch. The results were, in one case, 5.95 per cent., and in the second, 16.4 per cent., in excess.

Some of these results are collected in Table VII.

TABLE VII.

| Exp. | Nitre found. | Nitre per cent. |
|------|--------------|-----------------|
| 1. | 23·26 | 116·30 |
| 2*. | 23·04 | 115·20 |
| 3†. | 22·21 | 111·70 |
| 4‡. | 22·40 | 112·00 |
| 5§. | 19·09 | 95·45 |
| 6§. | 19·14 | 95·70 |
| 7. | 20·14 | 100·70 |
| 8. | 20·05 | 100·25 |
| 9 . | 18·21 | 91·05 |

No other mode of accounting for the excess could at first be imagined, than to attribute it to the production of some soda from the chloride of sodium by the action of the carbon, and possibly a little moisture, at the high temperature produced by the deflagration; but a number of experiments, made under circumstances which were assimilated as nearly as possible to those of the deflagrations with nitre, showed that the slight amount of decomposition suffered by the chloride of sodium in a deflagration is quite insufficient practically to influence the results.

It next became necessary to examine the action of the standard acid upon the solution, coloured with litmus, in order to ascertain if any source of error could there be traced.

In some instances, when the solution had been neutralised before boiling, it was observed that the blue colour of the litmus returned when the liquid attained the boiling point, and that, even after repeated changes to red, by the addition of successive portions of acid the blue again made its appearance after boiling for some time.

1. A solution of chloride of sodium coloured with litmus was reddened with a drop of sulphuric acid, and boiled for a considerable time, but without effecting any change in its colour.

2. 10 grains of carbonate of soda dissolved in water, and coloured with litmus, required in the cold, in order to produce the peculiar brownish-red tint due to strong acids, 84·8 measures

* In No. 2, 20·3 grs. of nitre were employed.

† In No. 3, 19·36 grs. of nitre were employed; the determinations were conducted, at a moderate heat, over gas.

‡ No. 4 was heated very gently over a spirit-lamp.

§ Nos. 5 and 6 were mixtures containing 95 per cent. of nitre.

|| No. 9 was a mixture containing 90 per cent. of nitre.

of the standard acid, corresponding to 9·58 grains of carbonate of soda. On boiling, the solution became perfectly blue. A second experiment gave the same result.

3. Several experiments were made in order to determine the difference between the amount of acid required to produce permanent redness in the cold, and subsequently, on boiling.

Table VIII. gives some of the results: —

TABLE VIII.

| Exp. | Measures of acid employed. | |
|------|----------------------------|---------------|
| | In the cold. | Upon boiling. |
| 1. | 65·80 | 68·20 |
| 2*. | 74·20 | 87·00 |
| 3. | 67·25 | 70·30 |
| 4. | 69·50 | 72·50 |
| 5. | 76·50 | 79·30 |
| 6. | 62·00 | 64·80 |
| 7. | 69·00 | 72·00 |
| 8. | 70·00 | 73·50 |
| 9. | 68·10 | 71·10 |
| 10. | 75·20 | 78·00 |
| 11. | 75·00 | 78·00 |
| 12. | 71·00 | 73·20 |
| 13. | 74·50 | 79·50 |
| 14*. | 85·00 | 91·00 |
| 15*. | 83·50 | 91·00 |
| 16*. | 83·50 | 87·20 |
| 17*. | 86·50 | 94·75 |

It will be seen that, in many of these determinations, the difference was scarcely greater than could be accounted for by the influence of the carbonic acid; and it was found that, in these cases, the amount of nitre indicated never exceeded the theoretical quantity; whereas, in those experiments which gave any considerable excess, a much greater amount of acid was required after the liquid was boiled.

An observation which had been made in several of the experiments seemed to throw some light upon this matter. It had been found that a very powerful ammoniacal odour was perceptible during the deflagration (even when all the materials had been carefully dried), and, on decomposing the alkaline solutions with

* These determinations were made with starch-charcoal.

sulphuric acid, a distinct odour of hydrocyanic acid was apparent, especially in cases where starch- or wood-charcoal had been used, and in which consequently an excessive result had been obtained.

The existence of cyanide of potassium in the fused mass was proved by qualitative experiments, and it appeared exceedingly probable that a certain quantity of cyanate of potassa was also formed, and by its subsequent decomposition furnished ammonia, whereby a larger quantity of sulphuric acid was neutralised than was actually required by the carbonate of potassa formed.

For the investigation of this question, a number of experiments were instituted with pure cyanide of potassium and cyanate of potassa.

9.545 grs. of pure cyanide of potassium, exposed for some time *in vacuo*, were dissolved in water; the solution was coloured with litmus, and very dilute sulphuric acid of known strength added, until the bright red colour was produced.* The amount of acid added corresponded to 9.31 grs. of cyanide of potassium. The solution was unchanged by boiling, and contained no ammonia.

9.64 grs. of cyanide of potassium were ignited for five minutes in a partially closed platinum crucible. Effervescence was observed in the fused mass. On dissolving in water, and adding the standard sulphuric acid to the solution coloured with litmus, the latter assumed the violet colour, when a quantity of the standard acid had been added, corresponding to 4.23 grs. of SO_3 . To produce the bright red tinge, 4.48 grs. of SO_3 were required. On boiling the solution, it became decidedly blue, and required (in all) to produce permanent red colour, 6.84 grs. of SO_3 . Abundance of sulphate of ammonia was detected in the boiled solution.

It will be observed that in this experiment a certain quantity of acid was required to convert the violet tinge into the bright red, which would indicate the formation of some carbonate of potassa, which was also indicated by the effervescence observed during the fusion of the cyanide. The very large quantity of the standard acid which was required to restore the red colour to the solution which had been rendered blue by boiling, denoted the presence of

* This experiment, as well as others made in a similar manner, showed that the hydrocyanic acid liberated produced no effect on the colour of litmus, the blue passing at once into bright red, without the intermediate violet stages seen in the case of carbonic acid. It was found, by direct experiment, that a solution of hydrocyanic acid added to blue litmus produced a similar effect to that of free carbonic acid, but that it had no effect upon the litmus when cyanide of potassium was present.

a considerable quantity of cyanate of potassa, which was confirmed by the subsequent detection of ammonia in the liquid.

10 grs. of pure carbonate of soda were mixed with 1.77 grs. of cyanide of potassium, and fused for five minutes in a partially closed crucible. To produce the violet tinge, 5.72 grs. of SO_3 were necessary; to convert this into the red, required 8.37 grs. of SO_3 . The solution became perfectly blue when boiled, and required (in all) 8.95 grs. of SO_3 to produce a permanent red colour.

The bearing of this experiment upon the determination of nitre will be rendered evident if it be remembered that the quantity of that salt equivalent to the carbonate of soda and cyanide of potassium employed is 22.14 grs. The amount of nitre, calculated from the alkalinity determined *in the cold*, would have been only 21.15 grs., or 95.5 per cent.; while, calculated from the result obtained on boiling, it would have been 22.62 grs., or 102.1 per cent.

9.86 grs. of cyanide of potassium were mixed with 5 grs. of lamp-black, covered with a layer of that substance, and heated to redness for five minutes. The product required, in the cold, 4.87 of SO_3 , to produce the violet tinge, 5.03 for the bright red, and 6.44 on boiling.

9.29 grs. of cyanide of potassium were heated, as before, with 5 grs. of lamp-black, but without any superficial layer. The product required, in the cold, 4.64 grs. of SO_3 for the production of the violet tinge, 4.8 for the bright red, and 6.34 on boiling.

In these experiments, the amount of cyanate produced is considerably diminished by the presence of the charcoal, and hardly any carbonate appears to be formed, the carbon being oxidised by the air in preference to the cyanate of potassa.

10.052 grs. of cyanide of potassium were mixed with 5 grs. of starch-charcoal, and heated as before. The mass fused completely in this instance. Its solution required, in the cold, to produce the violet tinge, 5.20 grs. SO_3 ; for the bright red, 5.62; and, on boiling, 7.01 to produce the permanent tinge.

9.403 grs. of cyanide of potassium were mixed with 20 grs. of starch-charcoal, and heated as usual. The mass only fused slightly at the bottom of the crucible. Its coloured solution was rendered violet, in the cold, by 4.7 grs. of SO_3 ; red, by 5.13 grs.; and required, on boiling, in all, 5.75 grs. SO_3 .

These experiments render it sufficiently obvious that the presence of a considerable quantity of charcoal does not prevent the oxidation of the cyanide of potassium.

10.533 grs. of cyanide of potassium were mixed with 100 grs. of chloride of sodium and 20 grs. of starch-charcoal, and heated to redness for about five minutes. The mass had not fused, but merely agglutinated. Its aqueous solution, when coloured, required for the production of the violet tinge, 5.23 grs. of SO_3 ; for the bright red, in the cold, 5.75; and, upon boiling, for the permanent red colour, 7.08 grs. SO_3 .

10.803 grs. of cyanide of potassium were mixed with 5 grs. of lamp-black and 120 grs. of chloride of sodium, and heated to redness for five minutes. The mass had fused. Its coloured solution became violet on addition of 5.55 grs. of SO_3 ; red, in the cold, with 5.83; and required, in all, for the production of the permanent red, upon boiling, 7.4 grs. SO_3 .

In these cases, the conditions of the experiments were as nearly as possible the same as those under which the determinations of nitre were made. It will be seen that, under these circumstances, the production of cyanate was also very considerable.

It was expected that the oxidation of the cyanide of potassium, in cases where starch-charcoal was employed, would have been much greater, since, in the nitre determinations with starch-charcoal, a much larger excess was always obtained. In the case of the actual deflagration, however, the temperature was much higher where starch charcoal was used, on account of the very much smaller volume of that substance. Probably, under these circumstances, the conditions for the formation of cyanate would be more favourable.

Cyanate of potassa itself was next subjected to experiment.

20 grs. of cyanate of potassa were dissolved in cold water, the solution coloured with litmus, and treated with dilute sulphuric acid of known strength. The addition of the first few drops produced the peculiar wine-red colour. 3.28 grs. of SO_3 were added before the red shade was produced in the cold. On boiling the solution, it became quite blue; and this phenomenon was repeated after several successive additions of sulphuric acid, until 14.24 of SO_3 , in all, had been added.

In a second experiment with the same quantity of cyanate of potassa, 3.28 grs. of SO_3 were required in the cold; 14 grs., in all, were finally required upon boiling the solution.

In both of these experiments the odour of cyanic acid was distinctly perceived upon the addition of sulphuric acid, showing that a considerable quantity of this acid escapes decomposition, although the excess of the sulphuric acid employed above that required to

neutralise the potassa shows that the presence of cyanate in the fused mass after deflagration would cause a considerable apparent excess of nitre to be obtained.

Although, in several instances where a considerable excess had been obtained, notable quantities of ammonia were detected in the neutralised solutions, concentrated by evaporation, it was deemed essential to obtain more direct evidence of the existence of cyanate of potassa in the products obtained by the deflagration of such a mixture as had on a former occasion furnished the greatest excess.

20 grs. of nitre, 20 of starch-charcoal, and 80 of salt were deflagrated in the usual manner. The agglutinated mass was finely pulverised, and digested twice for some minutes with strong alcohol. The insoluble portion was separated by filtration, washed with alcohol, and afterwards completely extracted with water. The alcoholic solution was evaporated, the residue dissolved in water, and the solution treated with sulphuric acid.* It became red, in the cold, upon the addition of 1 measure of acid; the blue colour, however, returned upon boiling, and 4·5 measures in addition were required. The aqueous solution was also treated as usual with the standard acid; it required 82·5 measures of acid in the cold, but became blue on boiling, and required 4·5 measures in addition. The quantity of nitre, inferred from the total amount of acid employed, was 20·73 grs., or 103·65 per cent.

Another experiment was made in the same manner; but in this case there was hardly any additional quantity of sulphuric acid required after boiling, indicating that, from some accidental circumstance, hardly any cyanate had been produced. In this instance, moreover, the quantity of nitre obtained corresponded as closely as could be expected with the theoretical quantity.

In a third experiment, the result closely resembled that obtained in the first.

In a fourth experiment, 21·38 grs. of nitre were obtained, or 106·9 per cent.

The cause of the excess having been satisfactorily ascertained to be the formation of cyanate of potassa, and the neutralisation of a portion of the sulphuric acid by the ammonia formed from the cyanate, some experiments were made with a view to obviate this cause of error, by an alteration in the conditions under which the deflagration was effected.

In some cases, the mixture was projected by degrees into a red-

* The acid used in these experiments contained 8·93 grs. of SO_3 in 100 measures.

hot crucible. In most of these, a considerable deficiency was obtained, owing to the carbon having been partly consumed without acting on the nitre. In only one instance, in which 5 grs. of wood-charcoal were employed, the result showed a considerable excess. No accurate results were obtained by the use of a protecting film of carbon during the deflagration, which confirmed the conclusions drawn from the direct experiments with cyanide of potassium.

The great object to be attained appeared to be the introduction of so powerful a reducing agency into the deflagrating mass, as should at the same time ensure the complete deoxidation of the nitre, and prevent the conversion of any cyanide of potassium into cyanate of potassa. A compound containing hydrogen and carbon appeared likely to fulfil these conditions, and recourse was at once had to resin, as being the substance best adapted for the purpose.

In carrying out this idea, considerable difficulties were experienced in adjusting the proportion of resin, and the degree of heat to be employed.

When 10 grs. of resin were employed for 20 of nitre (with 120 of salt), and the mass heated over an argand burner, a considerable quantity of cyanate of potassa was found in the solution, and yet only 14.94 grs. of nitre were indicated by the standard (hydrochloric) acid. The remainder of the nitre which had escaped deoxidation was determined by evaporating the solution, and igniting the residue with lamp-black. The deficiency was thus supplied. It would appear that, in this case, so much of the carbon and hydrogen were volatilised in an unoxidised state, that a sufficient quantity was not left to effect the deoxidation of the nitre.

When 20 of resin were employed, no cyanate was found in solution, but the quantity of nitre indicated was only 19.27 or 96.35 per cent.

It was supposed probable that a reduction of the proportion of chloride of sodium would have the same effect as increasing the quantity of resin, by concentrating its action upon the nitre. With this view, 80 grs. of chloride of sodium and 20 of resin were employed in the next experiment, but only 18.3 grs. of nitre, or 91.5 per cent., were obtained.

Since it appeared that, in this experiment, the moderate heat applied volatilised a great part of the resin before the temperature was sufficiently high to allow of deflagration, another experiment was made with 30 grs. of resin and 80 of chloride of sodium, and the crucible was at once heated to bright redness over the

Herapath blowpipe. But, in this case, only 16·15 grs. of nitre were obtained, or 80·75 per cent.

50 grs. of resin and 80 of salt were then employed, and the mixture heated over a gauze burner. A small quantity of cyanate was found in the solution, and the acid used indicated 20·24 grs. of nitre, or 101·2 per cent.

When 30 of resin and 100 of chloride of sodium were heated over a gauze burner, a considerable quantity of cyanate was found in the solution, and the alkalinity obtained corresponded to 21·53 grs. of nitre, or 107·65 per cent.

Another experiment, in which the proportion of salt was increased by 20 grs., gave exactly the same result.

The salt was now diminished to 80 grs., with the same proportion of resin, and the mass was heated to redness for one minute after all vapours had been evolved. A considerable quantity of cyanate was here found, and the result gave 20·78 of nitre, or 103·9 per cent.

A second experiment gave the same result.

Since so much cyanate of potassa was produced in these cases, it was deemed advisable not to prolong the application of heat after the deflagration had finished, and the experiments included in Table IX. exhibit the results which were obtained when the mixture was heated only as long as any vapour was disengaged.

TABLE IX.
(Nitre employed, 20 grs.)

| Exp. | Resin. | Salt. | Nitre found. | Nitre per cent. |
|------|--------|-------|--------------|-----------------|
| 1. | 20 | 120 | 19·74 | 98·70 |
| 2. | 20 | 120 | 20·02 | 100·10 |
| 3. | 25 | 120 | 20·02 | 100·10 |
| 4. | 20 | 100 | 19·81 | 99·05 |
| 5. | 30 | 80 | 19·99 | 99·95 |
| 6. | 30 | 80 | 20·01 | 100·05 |
| 7. | 30 | 80 | 19·98 | 99·90 |
| 8. | 30 | 90 | 19·90 | 99·50 |
| 9*. | 30 | 80 | 19·17 | 95·85 |
| 10*. | 30 | 80 | 19·17 | 95·85 |
| 11*. | 30 | 80 | 19·17 | 95·85 |
| 12. | 30 | 80 | 19·84 | 99·20 |
| 13. | 30 | 80 | 20·07 | 100·35 |

* In Nos. 9, 10, and 11, a mixture containing 95 of nitre, 3 of chloride of sodium, and 2 of sulphate of potassa, was employed.

An inspection of this Table will show that, although the results were generally pretty accurate, when 20 grs. of pure nitre were employed, there was still a tendency (especially where less than 20 grs. of nitre were taken, as in the impure samples) to the formation of cyanate, which was indicated by the action of the acid.

This observation suggested the expediency of trying a method whereby any chance of error resulting in the formation of cyanate might be obviated, by the addition, after deflagration, of a powerful oxidising agent, such as chlorate of potassa, whereby the conversion of the cyanate into carbonate might be effected. It appeared probable, at the same time, that the additional elevation of temperature, caused by the powerful action of the chlorate of potassa upon the unconsumed carbon, would exclude the possibility of nitre escaping conversion into carbonate.

In the first experiments in which chlorate of potassa was employed, the deflagration was conducted, according to the old method, with lamp-black, the chlorate being subsequently sprinkled over the mass, which was afterwards heated for two or three minutes to redness. The results of these experiments are exhibited in Table X.

TABLE X.

(Proportions employed : 20 of nitre, 5 of lamp-black, 80 of salt.)

| Exp. | Nitre found. | Nitre per cent. |
|------|--------------|-----------------|
| 1. | 19·82 | 99·08 |
| 2. | 20·14 | 100·70 |
| 3. | 20·02 | 100·10 |
| 4. | 20·07 | 100·35 |
| 5. | 19·96 | 99·80 |
| 6*. | 18·94 | 94·70 |
| 7*. | 18·94 | 94·70 |
| 8*. | 19·05 | 95·25 |
| 9*. | 18·94 | 94·70 |

The results obtained by this modification were very encouraging, and those furnished by the sample containing sulphate of potassa also showed that any chance of error arising from the formation of sulphide of potassium was also obviated by the use of chlorate of potassa.

In cases where much sulphate was present, it was found that

* These determinations were all made with a mixture containing 95 of nitre, 3 of chloride of sodium, and 2 of sulphate of potassa.

the deflagration caused by sprinkling the chlorate upon the mass was so violent as to endanger the projection of a portion of the fused mass. In addition, the length of time required to filter off the unconsumed carbon and to wash out all the alkali, formed a serious objection to the process, when applied for commercial purposes. The finely-divided state of the carbon rendered it impossible to effect the accurate determination of the alkalinity without previous filtration.

The experiments made with resin having shown that much less carbon was left unconsumed than in the case of lamp-black, and that the small residual portion was in an exceedingly porous condition, and therefore readily oxidised, an endeavour was made to take advantage of this circumstance in order to avoid the necessity for filtering.

A series of trials eventually led to the adoption of the following process, as yielding the most trustworthy results.

20 grs. of the sample to be examined are intimately mixed, in the platinum crucible, with 30 grs. of finely-powered resin, and 80 grs. of pure dry salt. The crucible is then loosely covered, and a moderate heat applied with a gauze burner; the heat is maintained for two or three minutes after all evolution of vapour has ceased. The crucible is then allowed to cool to such an extent that the chlorate of potassa shall not fuse when sprinkled upon the mass. About 25 grs. of the chlorate are added so as to form a layer upon the surface. A very gentle heat is first applied, until most of the chlorate has been decomposed, when the temperature is raised to bright redness, and maintained in that state for two or three minutes. The mass should then appear completely liquid, and free from any floating particles of carbon.*

When cool, the mass is carefully shaken out of the crucible into a funnel, and the crucible and cover washed with boiling water. The mass is dissolved by a stream of hot water from a washing bottle, and the solution allowed to run into the flask in which the determination is to be made. The liquid is coloured with litmus, and neutralised as usual with standard acid.

Table XI. includes the results of experiments made in this manner with pure nitre.

* It was found that those determinations in which any carbon was left always gave a marked excess.

TABLE XI.

| Exp. | Nitre found. | Nitre per cent. |
|------|--------------|-----------------|
| 1. | 20·00 | 100·00 |
| 2. | 20·00 | 100·00 |
| 3. | 19·97 | 99·85 |
| 4. | 19·97 | 99·85 |
| 5. | 20·08 | 100·40 |
| 6. | 20·08 | 100·40 |
| 7. | 20·08 | 100·40 |

Although, in the three last experiments, the error is hardly greater than would be permitted in such a process, it is obvious that accurate results would be obtained with greater certainty if the acid were graduated by determining the mean quantity required by 20 grs. of pure nitre, when deflagrated with the above precautions.

Some of the determinations, included in Table XII. of the amount of pure nitre contained in certain artificial mixtures, were calculated from the amount of standard acid employed in Nos. 5, 6, and 7 of Table XI.

TABLE XII.

| Exp. | Nitre found. | Nitre per cent. |
|------|--------------|-----------------|
| 1*. | 19 01 | 95·05 |
| 2†. | 17·81 | 95·45 |
| 3‡. | 17·90 | 89·50 |
| 4. | 17·86 | 89·30 |
| 5. | 18·01 | 90·05 |
| 6. | 17·97 | 89·85 |
| 7. | 17·97 | 89·85 |
| 8. | 18·01 | 90·05 |
| 9. | 17·99 | 89·95 |

Although the recent experiments made with this method have been most satisfactory, it could have been desired that more numbers might have been added to the above list. The accuracy of such a process can only be fully confirmed by extensive

* Nos. 1 and 2 were made with a mixture consisting of 95 of nitre, 3 of salt, and 2 of sulphate of potassa.

† In No. 2, only 18·655 grs. of the impure nitre were employed.

‡ Nos. 3 to 9 were made with a mixture consisting of 90 of nitre, 5 of salt, and 5 of sulphate of potassa.

practical application; and the authors hope, on a future occasion, to submit to the Society the results of such a trial.

It may not be out of place to direct attention to the most interesting of the general conclusions which have been arrived at, in the course of the above experiments.

1. That a considerable quantity of nitre may escape decomposition at a high temperature, even when intimately mixed with an excess of finely-divided carbon, and although vivid deflagration of another portion of the nitre had taken place in its immediate neighbourhood.

2. That, in the deflagration of a mixture of nitre, salt and charcoal, binoxide of nitrogen is evolved in large quantity; an observation which has also been incidentally made in the case of far more energetic deflagrations. .

3. That a considerable quantity of cyanide of potassium is formed in these deflagrations, and that, even where much care had been taken to remove moisture from the materials employed in the experiments, a notable quantity of ammonia was evolved. An attempt, suggested by this circumstance, was made to determine nitre by ignition with charcoal and soda-lime, when the greater part of its nitrogen was obtained in the form of ammonia.

4. That the oxidation of cyanide of potassium by exposure to air at a high temperature is not prevented by the presence of carbon in a finely-divided state, or even by covering it with a layer of carbon.

The relations of nitre to different forms of carbon at a high temperature appear to present so many points of interest, whether viewed in relation to theory or to practice, that the authors have resolved to devote their earliest leisure to the investigation of the subject.

VI.—*Note on a New Method of Making Ferricyanide of Potassium and a Paracyanogen Compound.*

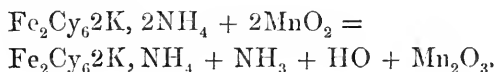
By LYON PLAYFAIR, C.B., F.R.S.

THIS note refers to two processes which only deserve description because they are of an unusual kind, and may possibly be employed for other purposes.

I.—*Ferricyanide of Potassium.*—When yellow prusside of potassium is precipitated by salts of lime or baryta, well-known sparingly soluble precipitates are obtained, containing 2 equivalents of barium or of calcium, instead of 2 equivalents of potassium. If R represent either of these metals, the formula of the precipitate is $\text{Fe}_2\text{Cy}_6, \text{K}_2\text{R}_2$. When these precipitates are treated with carbonate of ammonia, the earthy carbonates fall, and a solution is obtained of a salt $\text{Fe}_2\text{Cy}_6, 2\text{K}, 2\text{NH}_4$.

When this latter yellow salt containing ammonia is boiled with peroxide of manganese finely divided, ferricyanide of potassium is abundantly formed; and after the ebullition has been continued for some time, a portion of the solution filtered will be found to give no further precipitate with perchloride of iron, being wholly converted into a ferricyanide. During the boiling with the peroxide of manganese, ammonia is freely given off. The salt formed by this process in solution has all the properties of a ferricyanide, and would obviously be $\text{Fe}_2\text{Cy}_6, \text{K}_2\text{NH}_4$, in which 1 equivalent of ammonium replaces 1 equiv. of potassium in the red prusside. But this salt, by prolonged boiling with peroxide of manganese, is further decomposed, a green-coloured precipitate occurring, while the salt in solution still retains the ordinary characters of a ferricyanide, but contains less ammonium, more potassium, and generally an excess of iron. A salt of silver made from the red solution, and possessing the ordinary characters of the ferricyanide of silver, gave on analysis 10·89 per cent. of iron, and 60·28 per cent. of silver: calculation gives 10·44 per cent. of iron, and 60·45 per cent. of silver. This analysis leaves no doubt as to the character of the variable red salt in solution, though it contains, like the latter, an excess of iron.

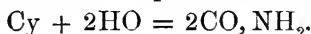
The formation of the ferricyanide is clearly owing to an oxidation of the ammonium.



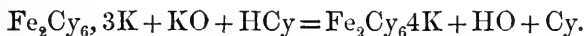
It is well known that when ferricyanide of potassium is boiled with ammonia, a ferrocyanide is produced, 1 equiv. of hydrogen replacing 1 equiv. of potassium in the ordinary yellow salt. The presence of an excess of peroxide of manganese in the reaction now described appears to prevent this decomposition, as ammonia is given off during the whole oxidation.

I do not describe this formation of ferricyanide as an economical process for procuring the salt, but as an instance of an unusual process of oxidation which may be applied to other purposes.*

II.—*Paracyanogen Compound*.—In making the nitroprussides, I had found that, when cyanogen was in the nascent state, it combined with 2 equivalents of water, and produced oxamide:



Either this substance or paracyanogen might, therefore, be expected from hydrocyanic acid if the hydrogen were subjected to oxidation. For this purpose, 1 equiv. of ferricyanide of potassium was mixed with an equivalent of potash; and to this mixture was added an equivalent of hydrocyanic acid, the purpose being to liberate the cyanogen under favourable circumstances. The reaction expected was as follows:—



On adding the hydrocyanic acid to the mixture of red prusside and potash, the solution becomes yellow in colour, but soon passes to a dark red, or even black colour,—a bulky precipitate of a similar colour falling down. During this action, a small quantity of gas is observed to escape. The formation of the precipitate is much favoured by the solutions being warm: when they are dilute, it is even necessary to raise them nearly to the boiling point.

The bulky reddish-black precipitate is collected on a filter, and washed with cold water, in which it is scarcely soluble. It dissolves readily in water containing caustic soda or potash, and may

* Ferricyanide of potassium may also be procured under the following circumstance, which deserves inquiry, as the reaction must be somewhat complicated. Common prusside of copper has the formula $\text{Fe}_2\text{Cy}_6, 3\text{CuK}$. When this salt is treated with caustic ammonia in the cold, a very pale red-coloured solution is obtained, which, boiled with peroxide of manganese, gives ordinary ferricyanide of potassium. Analysis gave the following results:—

- I. 12.26 grains gave 3.00 peroxide of iron, and 9.605 sulphate of potash.
 II. 14.225 grains gave 3.49 peroxide of iron, and 11.19 sulphate of potash.

| | I. | II. | Calculated. |
|---------------|-------|-------|-------------|
| Iron . . . | 17.12 | 17.17 | 17.02 |
| Potassium . . | 35.11 | 35.26 | 35.56 |

be purified in this way from a small quantity of oxide of iron which may fall down with it: it is again precipitated from the alkaline solution by the addition of an acid.

The precipitate contracts much in bulk during drying. It loses about $10\frac{1}{2}$ per cent. of water at 212° . Specimens obtained at different times did not give constant results.

| | First Preparation. | | Second Preparation. | | Third Preparation. |
|------------|--------------------|--------|---------------------|--------|--------------------|
| | I. | II. | I. | II. | |
| Carbon . | 40.050 | 40.240 | 42.053 | 42.415 | 38.918 |
| Nitrogen . | 41.618 | — | 42.772 | — | — |
| Hydrogen . | 3.400 | 3.393 | 3.324 | 3.318 | 3.252 |
| Oxygen . | 14.932 | — | 11.851 | — | — |
| | <hr/> 100.000 | | <hr/> 100.000 | | |

From these analyses it is obvious that the compound is not simply paracyanogen. Not only is the carbon in too large proportion to the nitrogen, but the hydrogen is more than sufficient to convert the oxygen into water. In the preparation of the substance, a little gas is always observed to escape,—due, probably, to the oxidation of a portion of the paracyanogen. The substance as prepared is therefore impure, and requires proper inquiry.*

Not being able, without interfering with another investigation, to pursue the subject further, in the very limited time which I have at my disposal for scientific pursuits, Baron Liebig has kindly placed it in the hands of one of his pupils for investigation.

* I find that the same substance can be procured by passing chlorine through cyanide of potassium. Purified by solution in soda, precipitation by hydrochloric acid, and washing, two preparations dried at 212° gave the following results on analysis :—

| | First Preparation. | | Second Preparation. |
|------------|--------------------|--------|---------------------|
| | 36.22 | 35.200 | |
| Carbon . | 36.22 | 35.200 | 35.200 |
| Nitrogen . | — | 42.300 | — |
| Hydrogen . | 3.150 | 3.000 | 3.030 |
| Oxygen . | — | 19.500 | — |
| | <hr/> 100.000 | | |

In this case, the carbon and nitrogen are nearly in the proportion to form cyanogen, but the hydrogen is in excess to the oxygen on the supposition that it was present as water. It should be mentioned that, on treating this black compound with nitric acid, a yellow substance is obtained, which, as I have only made one analysis, I do not venture to describe.

VII. — *On the Sulphovicates; and on Amylophosphoric Acid and the Amylophosphates.*

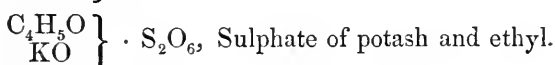
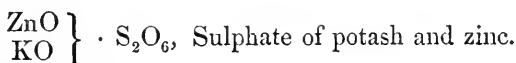
By FREDERICK GUTHRIE, B.A., Ph.D.

ASSISTANT IN THE LABORATORY OF OWEN'S COLLEGE, MANCHESTER.

WITH respect to the rational constitution of the sulphovicates, chemists are at present so far agreed as to admit in them the presence of sulphuric acid. An objection was formerly raised to this view, on the ground that the sulphuric acid could not be shown to exist, as such, by means of the usual reagents; and it was assumed that the salts in question contained hyposulphuric acid. This position has, however, been overthrown, partly by the discovery of isethionic acid, partly by the observed behaviour of other compounds of ethyl, such as the chloride and sulphide of ethyl, in which the chlorine and sulphur are much more difficult to recognise by means of nitrate of silver than is the case with the soluble inorganic compounds of these bodies.

A question, however, which still has to be answered, is — “In what manner do the sulphovicates contain the sulphuric acid?”

Those chemists who look upon sulphuric acid as a bibasic acid, and express the composition of its hydrate by the formula $2\text{HO}, \text{S}_2\text{O}_6$, view, for the most part, the salts of sulphovinic acid as basic sulphates, one of whose atoms of base is potash, and the other oxide of ethyl. They accordingly class sulphovinate of potash with the so-called double salts of sulphuric acid, such as the potassio-sulphate of zinc.



Now, in the first place, this view is contradicted by the fact that the oxide of ethyl in the second of these salts cannot be driven out by a more powerful base, as is the case with its analogue, the oxide of zinc, in the inorganic sulphate. Even on continued boiling with potash, the ether is not given off as alcohol. The difficulty of maintaining this view, again, is materially increased when we reflect that in the neutral sulphate of ether, $\left. \begin{array}{l} \text{C}_4\text{H}_5\text{O} \\ \text{C}_4\text{H}_5\text{O} \end{array} \right\} \cdot \text{S}_2\text{O}_6$, the one atom of ether may be eliminated or exchanged for water

or a base much more easily than the other, and that the so-called neutral ethers, such as acetic, nitric, or oxalic ether, on being boiled with caustic potash, are transformed, under formation of alcohol, into the potash salts of the corresponding acids.

These considerations render it more than doubtful whether the metallic oxide and the oxide of ethyl be equally basic in function. It seemed desirable that new facts should be gained for the elucidation of this point. I imagined that such facts might be furnished by the behaviour of an aqueous solution of a sulphovinate towards the galvanic current. For if, in the sulphovinate of potash, both the potash and ether be united as base with the sulphuric acid, we should be justified in expecting, on electrolysing a concentrated aqueous solution of this salt, that, at the + pole, sulphuric acid and oxygen would be liberated, and, at the - pole, potassium, (potash and hydrogen), together with ethyl, (or ether or some ethyl compound, possibly hydride of ethyl).

Into a cold, concentrated, aqueous solution of sulphovinate of potash, free from sulphate of potash, I accordingly introduced two platinum electrodes in such manner that they were separated by a porous clay cell. The electric current from four of Bunsen's carbo-zinc elements was sufficient to effect a lively disengagement of gas at both poles, accompanied by an evolution of heat which rendered cooling from the exterior necessary. In a short time the liquid surrounding the + pole showed a strong acid reaction. The gas which was here liberated smelt distinctly of aldehyde, and consisted of oxygen and carbonic acid. The liquid at this pole gave, with chloride of barium, a white precipitate which was insoluble in hydrochloric acid. Sulphuric acid was therefore present in the free state. At the same time, the liquid at the - pole assumed an alkaline reaction, and the gas there liberated proved to be pure hydrogen. I satisfied myself, by careful examination, of the entire absence of all carboniferous gases, nor could I detect at this pole the slightest traces of ether or alcohol.

It was imagined that the sulphuric acid and the aldehyde, which appeared at the + pole, might be secondary products of decomposition, effected by the oxygen, *in statu nascenti*. To get rid of this secondary decomposition, I formed the + pole of amalgamated zinc. On completing the circuit, a lively disengagement of gas took place at the - pole, as before, while, on the other hand, at the + pole, no gas at all was liberated, and neither aldehyde nor sulphuric acid were formed. The zinc electrode, however, soon became covered with a pellicle of sulphovinate of zinc, which, after

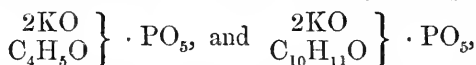
a time, broke the electric current. Again, a fresh solution being taken, the liquid at the + pole was made strongly alkaline with carbonate of potash. On the introduction of platinum electrodes, carbonic acid was plentifully liberated at the + pole, but as no sulphate of potash could be detected, it followed that this was due to the liberation not of sulphuric, but of sulphovinic acid.

In the same manner, making use of platinum electrodes, I electrolysed an aqueous solution of amylo-sulphate of potash, and recognised precisely analogous phenomena. At the + pole, oxygen was liberated and a distinct smell of valerianic acid noticeable. The solution around this pole became acid, and contained sulphuric acid. At the - pole, the liquid became distinctly alkaline, and the gas there liberated was, as before, pure hydrogen. The slightest traces of fusel oil or amylic ether would at once have been recognised by their powerful odour, had they been separated. The liquid at the - pole remained inodorous.

From these experiments I believe the conclusion may legitimately be drawn, that, in amylosulphate and sulphovinate of potash, the oxides of ethyl and amyl have not the same function as the potash, but that they are combined with the sulphuric acid in a different, and, as it appears, a more intimate manner. The fact that, on electrolysis, these organic oxides remain with the sulphuric acid, and accompany it to the + pole, shows that the potash alone is the electropositive constituent of these salts, and that the formula $\left. \begin{matrix} \text{KO} \\ \text{C}_4\text{H}_5\text{O} \end{matrix} \right\} \cdot \text{S}_2\text{O}_6$ expresses a hypothesis on the constitution of sulphovinate of potash which rests upon false assumption.

It seemed to me of importance to examine in a similar manner the ethylophosphates, and to see whether in these the organic oxide is liberated at the + pole, as in the sulphovinates, or whether it goes to the - pole. For this purpose, the amylophosphate of potash was chosen, because, if the oxide or hydrated oxide of amyl were liberated, together with the metallic oxide, at the - pole, it would be at once recognised by the mere odour. On introducing the platinum electrodes into a concentrated aqueous solution of amylophosphate of potash, separated into two portions by a clay cell, hydrogen was liberated at the - pole, and oxygen, together with carbonic acid, at the + pole. The solution at the latter pole assumed an acid reaction, and smelt distinctly of valerianic or butyric acids (evidently secondary products of decomposition). The liquid at the - pole became alkaline, but remained odourless.

From this it would appear that in the amylophosphates, and, generally, in the ethylophosphates, we are not at liberty to assume that the organic oxides are combined in the same manner as the metallic oxides; that is, as base. Accordingly, we must not understand the ordinary formulæ for ethylo- and amylophosphate of potash,



as if the organic oxides played the same part in them as does the basic water in the ordinary tribasic phosphate of potash, $\left. \begin{matrix} 2\text{KO} \\ \text{HO} \end{matrix} \right\} \cdot \text{PO}_5$; but we must rather assume that the phosphoric acid, together with the oxide of amyl, forms a bibasic amylophosphoric acid.

As amylophosphoric acid and its salts have only lately become known, I subjoin a description of their preparation and properties.

AMYLOPHOSPHORIC ACID.

If about equal weights of hydrated phosphoric acid and hydrated oxide of amyl be shaken in a bolt-head till perfect mixture occurs, the two unite with considerable elevation of temperature, and the mixture assumes a pale red tinge. The mixture is allowed to remain for about twenty-four hours in a place of about 60° — 80° C. temperature. The liquid assumes a fine wine-red colour during this time, and the formation of amylophosphoric acid takes place. It is now to be repeatedly shaken with warm water, which removes the amylophosphoric acid, together with the free phosphoric acid, from the uncombined fusel-oil. The wash-waters are collected, slightly supersaturated with carbonate of potash, and evaporated on a water-bath almost to dryness. The mass obtained in this manner consists of amylophosphate of potash, together with phosphate and traces of carbonate of potash. To get rid of the last two, the mass is digested with warm spirits of wine and quickly filtered. The phosphate and carbonate of potash remain for the most part on the filter, while the amylophosphate of potash is in the filtrate. The filtrate is now evaporated almost to dryness upon a water-bath. This process has to be frequently repeated, stronger spirits being employed each time, and at last absolute alcohol, the last filtration being performed with the exclusion of air. The separation is only complete when a portion of the almost dry mass, dissolved in water, gives a snow-white precipitate with nitrate of silver.

The substance obtained as above is a yellowish, gelatinous,

transparent body, still containing combined alcohol. To get rid of this alcohol, it is sufficient to dissolve the mass repeatedly in water, and to evaporate to dryness on a water-bath. A honey-coloured mass is thus obtained, consisting of minute crystals of pure amylophosphate of potash.

This salt is a tenacious, finely crystallised, translucent body, without odour, but having the well-known peculiar taste of the other compounds of amyl. On exposure to the air, it absorbs moisture, and deliquesces to a syrupy transparent liquid of feeble smell. If it be dried, as far as possible, on a water-bath, and then heated in a tube by itself, or with hydrate of potash, it yields fusel-oil. Heated on platinum foil in the flame of a lamp, it burns with a pure white flame, leaving pyrophosphate of potash as residue. This decomposition is accompanied by a striking inflation of the mass, due probably to the escape of mechanically and chemically combined water. Amylophosphate of potash is soluble in every proportion in hot and cold water; it is soluble also in alcohol, but insoluble in ether. On account of the difficulty of freeing it completely from water, I have not subjected it to analysis. From the composition, however, of the salts formed from it, its composition doubtless corresponds with the formula $\left. \begin{matrix} 2\text{KO} \\ \text{C}_{10}\text{H}_{11}\text{O} \end{matrix} \right\} \cdot \text{PO}_5$.

As most of the amylophosphates are insoluble, or difficultly soluble, they may be readily prepared from the potash-salt by double decomposition. They are, in general, somewhat more soluble than the corresponding salts of tribasic phosphoric acid, and because the latter is unquestionably the more powerful acid; it may be completely removed by fractional precipitation, if its presence in the amylophosphate be suspected. Those salts which are insoluble in water are, like the phosphates, easily soluble in dilute nitric and hydrochloric acids. The amylophosphates are, generally speaking, more stable than the sulphovinates and ethylophosphates, inasmuch as they bear boiling with water without decomposition.

Amylophosphate of Lead, $\left. \begin{matrix} 2\text{PbO} \\ \text{C}_{10}\text{H}_{11}\text{O} \end{matrix} \right\} \text{PO}_5$, is precipitated from a dilute solution of amylophosphate of potash on the addition of acetate of lead. The precipitate, carefully washed and dried at 100°C ., is a bulky white powder, without taste or smell; it is easily soluble in hydrochloric and acetic acid. It contains no water. On analysis it gave the following result:—

a. 0.6335 grm. of the salt, dried at 100°C ., was treated with

fuming nitric acid, in order to effect decomposition; the mass was then dissolved in water, and the lead precipitated by hydrosulphuric acid. The phosphoric acid in the filtrate was precipitated as ammonio-phosphate of magnesia. The lead determination was lost. The weight of the pyrophosphate of magnesia was 0.2034 grm., corresponding to 0.1290 grm. phosphoric acid.

b. 0.6772 grm. dried at 100° C. was ignited in a porcelain crucible, treated with fuming nitric acid, and warmed, then boiled with water, and the lead precipitated by sulphuric acid. Alcohol being added, the whole was filtered, the filtrate boiled, and the phosphoric acid estimated as pyrophosphate of magnesia. The above quantity yielded 0.5507 grm. sulphate of lead, or 0.3764 grm. lead; and 0.2163 grm. pyrophosphate of magnesia, or 0.1373 grm. phosphoric acid.

c. 0.4834 grm. dried at 100° C. was burned with oxide of copper, pieces of previously fused chlorate of potash being introduced at the end of the tube, and copper turnings being placed in the anterior. On account of the small relative quantity of organic matter present, it is advisable to employ five or six decigrammes. The above quantity gave 0.2474 grm. carbonic acid, or 0.0749 grm. carbon; and 0.1419 grm. water, or 0.0157 grm. hydrogen.

The composition *per cent.*, as found and calculated, is accordingly—

| Calculated. | | Found. | | |
|-----------------|---------|-----------|-----------|-----------|
| | | <i>a.</i> | <i>b.</i> | <i>c.</i> |
| 2Pb | = 55.39 | — | 56.4 | — |
| C ₁₀ | = 16.02 | — | — | 15.5 |
| H ₁₁ | = 2.93 | — | — | 3.2 |
| PO ₅ | = 19.23 | 20.4 | 20.2 | — |
| O ₃ | = 6.43 | — | — | — |
| <hr/> | | | | |
| 100.00 | | | | |

Amylophosphate of Silver, $\left. \begin{matrix} 2\text{AgO} \\ \text{C}_{10}\text{H}_{11}\text{O} \end{matrix} \right\} \cdot \text{PO}_5$, is precipitated from a solution of amylophosphate of potash, on the addition of nitrate of silver, as a white bulky precipitate. The pure white colour of this combination is, as mentioned before, a good means for testing the purity of the potash-salt. Exposed to the light, this silver salt becomes grey; it remains white in the dark. It is appreciably soluble in warm water, but does not separate in the crystalline form on cooling. On long continued boiling with water it is decomposed, silver being deposited. Heated on a platinum foil it be-

comes yellow, leaving for residue pyrophosphate of silver. The salt employed for analysis was dried at 100°C .

a. 0.6404 grm. was ignited in a porcelain crucible with previously fused nitrate of potash. The mass thus obtained was drenched and digested with dilute nitric acid. From the clear solution thus obtained the silver was precipitated with hydrochloric acid, and the phosphoric acid with sulphate of magnesia and ammonia. In this manner 0.4782 grm. chloride of silver ($=0.3599$ grm. silver), and 0.1842 grm. pyrophosphate of magnesia ($=0.1169$ grm. phosphoric acid) were obtained.

b. 0.5631 grm. treated as above yielded 0.4198 grm. chloride of silver ($=0.3159$ grm. silver), and 0.1612 grm. pyrophosphate of magnesia ($=0.1023$ grm. phosphoric acid).

c. 0.4072 grm., burnt with oxide of copper with the same precautions as with the lead salt, gave 0.2300 grm. carbonic acid and 0.1197 water ($=0.0627$ grm. carbon and 0.0133 hydrogen).

d. 0.4204 grm. gave 0.2340 grm. carbonic acid and 0.1260 water ($=0.0638$ grm. carbon and 0.0140 grm. hydrogen).

Hence the following composition *per cent.* :—

| Calculated. | | Found. | | | |
|-----------------|---------|-----------|-----------|-----------|-----------|
| | | <i>a.</i> | <i>b.</i> | <i>c.</i> | <i>d.</i> |
| 2Ag | = 56.39 | 56.19 | 56.10 | — | — |
| C ₁₀ | = 15.66 | — | — | 15.39 | 15.18 |
| H ₁₁ | = 2.87 | — | — | 3.26 | 3.33 |
| PO ₅ | = 18.78 | 18.26 | 18.16 | — | — |
| O ₃ | = 6.20 | — | — | — | — |
| <hr/> | | | | | |
| 100.00 | | | | | |

Amylophosphate of Copper, $\left. \begin{matrix} 2\text{CuO} \\ \text{C}_{10}\text{H}_{11}\text{O} \end{matrix} \right\} \cdot \text{PO}_5$, is precipitated from a dilute solution of amylophosphate of potash on the addition of a dilute solution of sulphate of copper. The precipitate is at first almost perfectly white; it assumes after a time a bluish tinge, and in the dry state is a light blue amorphous powder. This copper salt may be heated to 110°C . without decomposition ensuing.

a. 0.7633 grm. was ignited, the mass obtained dissolved in hydrochloric acid, and the copper precipitated by hydrosulphuric acid. The washed sulphide was dried, and mechanically separated as perfectly as possible from the filter. The filter was burned, and its ash, together with the sulphide of copper, was treated with fuming nitric acid. After dilution, the sulphur was separated by filtration, and the copper precipitated by potash. The filtrate from

the sulphide of copper was boiled to expel the hydrosulphuric acid, and the phosphoric acid precipitated as ammonio-phosphate of magnesia. The above quantity gave 0.2691 grm. oxide of copper (=0.2149 grm. copper), and 0.3658 grm. pyrophosphate of magnesia (0.2323 grm. phosphoric acid).

b. 0.4366 grm. gave 0.4108 grm. carbonic acid (=0.1120 grm. carbon), and 0.1882 grm. water (=0.0209 grm. hydrogen).

| Calculated. | | Found. | |
|-----------------|---------|--------|------|
| | | a. | b. |
| 2Cu | = 27.70 | 28.1 | — |
| C ₁₀ | = 25.98 | — | 25.6 |
| H ₁₁ | = 4.76 | — | 4.8 |
| PO ₅ | = 31.16 | 30.4 | — |
| O ₃ | = 10.39 | — | — |
| <hr/> | | | |
| 100.00 | | | |

Amylophosphate of Baryta, $\left. \begin{matrix} 2\text{BaO} \\ \text{C}_{10}\text{H}_{11}\text{O} \end{matrix} \right\} \cdot \text{PO}_5$, is precipitated from a solution of amylophosphate of potash, on the addition of chloride of barium, in the form of white scales of a silky lustre. This salt is slowly precipitated from cold solutions; its formation, and especially the formation of the scales, is favoured by gentle heat. Although the specific gravity of the baryta-salt is doubtless greater than that of the copper compound, yet the former collects principally at the surface of the liquid,—a phenomenon which may possibly be ascribed to the fatty nature of the body.

For the determination of the baryta and the phosphoric acid, weighed portions of the substance were ignited, the residues digested with dilute nitric acid, and the liquid containing the baryta and phosphoric acid filtered from the carbon. The baryta was then precipitated by sulphuric acid, and the phosphoric acid as ammonio-phosphate of magnesia.

a. 0.4588 grm. gave 0.3473 grm. sulphate of baryta (=0.2043 grm. barium), and 0.1692 grm. pyrophosphate of magnesia (=0.1074 grm. phosphoric acid).

b. 0.5730 grm. gave 0.4358 grm. sulphate of baryta (=0.2565 grm. barium), and 0.2122 grm. pyrophosphate of magnesia (=0.1347 grm. phosphoric acid).

c. 0.4013 grm., burned as above with oxide of copper, gave 0.2796 grm. carbonic acid and 0.1531 grm. water (=0.0763 grm. carbon and 0.0170 grm. hydrogen).

Hence the following composition *per cent.* :—

| Calculated. | | Found. | | |
|-----------------|---------|--------|-------|-------|
| | | a. | b. | c. |
| 2Ba | = 45·07 | 44·54 | 44·76 | — |
| C ₁₀ | = 18·73 | — | — | 19·00 |
| H ₁₁ | = 3·62 | — | — | 4·24 |
| PO ₅ | = 23·68 | 23·4 | 23·5 | — |
| O ₃ | = 7·89 | — | — | — |
| <hr/> | | | | |
| 99·99 | | | | |

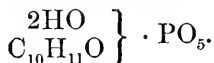
In a solution of subnitrate of mercury, amylophosphate of potash produces a precipitate in the form of a white amorphous powder, the composition of which has not been determined.

Amylophosphate of Ammonia, $\left. \begin{matrix} 2\text{H}_4\text{NO} \\ \text{C}_{10}\text{H}_{11}\text{O} \end{matrix} \right\} \text{PO}_5$. For the preparation of this salt, freshly precipitated amylophosphate of copper may be suspended in water and treated with freshly prepared sulphide of ammonium. The filtrate from the sulphide of copper is then boiled, again filtered, and evaporated to dryness on a water-bath. It is, however, in this process impossible to avoid the formation of sulphite and sulphate of ammonia. These impurities may be removed by recrystallisation from alcohol. In its external properties, the ammonia compound prepared as above has great similarity to the potash salt. The same body is obtained in a state of greater purity by the direct neutralisation of amylophosphoric acid by ammonia.

Amylophosphoric Acid.—For the preparation of free amylophosphoric acid, I made use of the freshly-prepared and well-washed copper salt. This salt was suspended in water, and the copper precipitated from it by a stream of hydrosulphuric acid. The liquid, filtered as quickly as possible from the sulphide of copper, reacted strongly acid; it was evaporated to the consistence of a syrup on a water-bath. A drop of this syrupy mass, dissolved in water and neutralised by ammonia, gave a pure white precipitate with nitrate of silver,—a proof that the acid had neither been decomposed by the precipitation of the copper nor by the evaporation on the water-bath. At this stage of concentration, the acid did not lose weight over sulphuric acid. After replacement on the water-bath, minute crystals were formed, which, under the microscope, proved to be long needles.

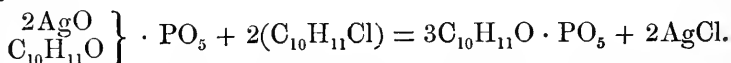
Amylophosphoric acid, prepared as above, is without odour, has

a strong acid taste, and easily expels carbonic acid from combination. It is soluble in water and alcohol, but insoluble in ether, so that it is precipitated on mixing a concentrated alcoholic solution with ether. The crystallised acid eagerly absorbs moisture from the air, and deliquesces: I was in consequence unable to procure a quantity of the dry acid sufficient for analysis. From the composition of its salts, however, we are justified in supposing its formula to be—



Amylophosphoric acid is distinguishable from ethylo- and amylo-sulphuric acids, as well as from ethylophosphoric acid, by its greater stability; inasmuch as the former three acids, even in dilute solution, are quickly decomposed on the application of heat, while the latter, in concentrated solution, bears the heat of a water-bath without undergoing decomposition. Heated in the flame of a lamp, it burns with a white flame, leaving a residue of phosphoric acid.

If dry amylophosphate of silver be introduced into a tube, moistened with a few drops of chloride of amyl, and the tube be then hermetically sealed and exposed for several hours to a temperature of about 180°C ., decomposition ensues. On the one hand, chloride of silver is found; and on the other, an ethereal liquid, which is taken up by alcohol, and reprecipitable therefrom in oily drops on the addition of water. The smell of this body is distinctly different from that of fusel-oil, as well as from that of chloride of amyl. It is probably amylophosphate of oxide of amyl, the formation of which may have occurred according to the equation:



Unfortunately, I had not sufficient of this body for analysis.

VIII.—*On the Action of Heat upon the Oxychloride of Copper (Atacamite.)*

By FREDERICK FIELD.

SOME time since a paper was published by me in the "Memoirs of the Chemical Society," "On the Composition of a Specimen of Atacamite from the province of Copiapo, Chili." As I have fre-

quently met with this mineral since in various parts of Atacama, and at different times have had large quantities to smelt, and opportunities of observing its behaviour under the influence of heat, I thought perhaps a few remarks would not be uninteresting, more especially as the results obtained by me upon this native oxychloride of copper differ considerably from those of Proust and others upon the artificially prepared compound.

In Gmelin's "Handbook of Chemistry," (Cavendish Society,) Vol. v. p. 440, under the head of "Mono-hydrated Oxychloride of Copper," it is said, upon the authority of Proust, that a compound having the composition $\text{CuCl}, 3\text{CuO}$ is obtained by gently heating the hydrated compound $\text{CuCl}, 2\text{CuO} + \text{HO}$, and that at a red heat oxygen is given off, and it is converted into a compound of protoxide and dichloride of copper, $\text{CuCl}, 3\text{CuO} = \text{Cu}_2\text{Cl}, 2\text{CuO} + \text{O}$. It is also called by Proust, p. 438, same volume, "Cupric oxide with cuprous chloride, the residue obtained by heating cupric oxychloride." In p. 441, same volume, the hydrated cupric oxychloride found in nature as atacamite when heated, according to the experiments of A. Vogel, gives off hydrochloric acid.* In the same page, the composition is given as under, viz. :—

| | |
|--------------------------|--------|
| Chloride of copper . . . | 30·17 |
| 3 Oxide of copper . . . | 53·72 |
| 4 Water . . . | 16·11 |
| | <hr/> |
| | 100·00 |

The mass of mineral upon which I experimented had, as nearly as possible, the same composition :—

| | |
|--------------------------|--------|
| Chloride of copper . . . | 30·94 |
| Oxide of copper . . . | 53·31 |
| Water . . . | 16·12 |
| | <hr/> |
| | 100·00 |

or $\text{CuCl}, 3\text{CuO} + \text{HO}$, which requires 15·87 per cent. chlorine, 16·11 per cent. water, and 57·29 per cent. oxide of copper. On placing 100 grs. of the above mineral finely powdered in a platinum crucible, and exposing it with every precaution for half an hour to a heat gradually increasing to whiteness, it was found on reweighing to have lost 46·32 grs. and appeared a deep black powder without any shade of brown or other colour. It will be seen from

* Vogel's observation appears rather to refer to the artificially prepared compound.

this that the loss on heating exactly corresponds with the sum of the water and chloride of copper the mineral originally contained, viz., 47·06 per cent. The residue should then consist of nothing but pure black oxide. It was dissolved in pure nitric acid, and tested for chlorine by nitrate of silver. A merely perceptible cloud of chloride of silver was obtained, which is accounted for by a trace of the sublimed chloride of copper remaining on the upper part of the crucible. The silver was separated by HCl, and the copper estimated in the usual way.

53·31 grs. gave 42·61 copper = 79·94 per cent.,
calculation being 80·00.

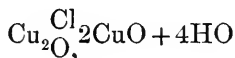
During the whole time of heating, a dense white smoke was developed, which condensed as a yellow powder when any cold surface was introduced. A glass rod, dipped in solution of ferrocyanide of potassium and held over the fumes, became instantly covered with the rose-coloured ferrocyanide of copper. I could not in these experiments collect sufficient of the sublimate for analysis. I had to operate upon a larger quantity. Two or three hundred-weight of specimens containing comparatively small portions of the oxychlorides (from 4 to 5 per cent.) were heated with a quantity of charcoal and wood shavings in a small furnace somewhat resembling a lime-kiln loosely covered. When the ore had become thoroughly red hot, white fumes arose, and condensed on the cover and the superior layer of mineral, as a brilliant yellow sublimate, highly crystalline in appearance. These were removed with great care, placed at once into a weighed stoppered glass bottle, and subjected to the heat of an air-bath. It was perfectly impossible to handle them or to expose them one moment to the colder air, as they turned at first snow-white, and then green, owing to absorbed water.

25 grains of this yellow sublimate were dissolved in water, and yielded upon analysis 13·13 chlorine and 12·86 copper = 52·52 per cent. of the former and 47·46 of the latter, or as nearly as possible pure anhydrous chloride of copper.

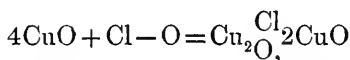
From the above experiments it appears that the chloride, when associated with the oxide of copper, comports itself in a different manner than when in its uncombined state, in the latter case being converted into dichloride with loss of chlorine; but even this compound is itself dissipated at a white heat. I am led to believe that in the decomposition of the oxychloride there is no intermediate stage in the process, such as the conversion of the protochloride

into the dichloride, but a direct disengagement of the former from its associated oxide, in the first place, because the characteristic flame is uniform throughout from the moment of heating, and in the second, because the evolved sublimate consists of pure anhydrous chloride of copper.

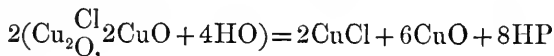
The following formula might be offered for oxychloride of copper, although I confess no experiments of mine have been able to prove that such is the fact.



We have here 2 equivs. of copper combined with 1 equiv. oxygen and 1 equiv. chlorine, and coupled with 2 equivs. of protoxide, so that 1 equiv. of chlorine might be supposed to have replaced 1 equiv. of oxygen in 4 equivs. of the oxide of copper,



and upon the application of heat, either two equivalents are acquired, or the atom may be supposed to be divided.



When the oxychloride is heated with lime, chloride of calcium is formed, together with black oxide of copper.

IX.—*Analysis of a Meteoric Stone from the Desert of Atacama.*

By FREDERICK FIELD.

THE following is an analysis of a meteoric stone which fell sometime since in Bolivia, about a hundred leagues from the coast North of the port of Cobiza. A portion sent me by a friend had a stony metallic appearance, was very hard and tough, of specific gravity 7.89. In various cavities upon the surface were minute crystals of a brownish white colour, which on analysis were found to contain silica, lime, oxide of iron, and phosphoric acid. A

portion broken off from the metallic part, and analysed, gave nickel, iron, phosphorus, and traces of cobalt; no vestige of sulphur could be detected. The following is the quantitative analysis—

| | |
|--------------|-------|
| Iron . . . | 87·80 |
| Nickel . . . | 11·88 |
| Phosphorus . | 00·30 |
| | <hr/> |
| | 99·98 |

with traces of cobalt.

The phosphorus was estimated as phosphate of magnesia. The sulphides of nickel and iron, dissolved in dilute aqua-regia, were separated by succinate of ammonia. The stone was perfectly soluble in dilute hydrochloric acid.

X.—*Some Experiments illustrative of the Reciprocal Decomposition of Salts.*

By J. H. GLADSTONE, Ph.D., F.R.S.

AMONG the conclusions arrived at by me in a paper published in the “Philosophical Transactions” of last year, were the following:—

“Where two or more binary compounds are mixed under such circumstances that all the resulting bodies are free to act and react, each electro-positive element arranges itself in combination with each electro-negative element in certain constant proportions.”

“These proportions are not merely the resultant of the various strengths of affinity of the several substances for one another, but are dependent also on the mass of each of the substances in the mixture.”

My impression is that these laws are of universal application; but this can be established only by the observation of a large number of varied instances in which they hold good, and by the investigation and explanation of every supposed exception.

The present paper contains the account of some reactions bearing upon the subject, which are of value, either from the experiments having been performed with elements hitherto untried, or from some novelty in the mode of observation. Every difficulty which,

to my knowledge, has been proposed by others, or which has occurred to my own mind, has been examined, and is here commented on.

Chromium Salts.—The soluble chromic salts have very remarkable optical properties. Their colour, by transmitted light, depends not only for its depth, but for its very character, upon the amount of salt which the ray has traversed in the solution. If the solution be weak, or if only a thin stratum be seen, it appears green; if a stronger solution or a thicker stratum, it appears red. As these two colours are complementary, or nearly so, the red on dilution passes into the green, not by a strictly speaking intermediate shade, but by a kind of brown or neutral tint. Now though, as far as I am aware, this description applies to all the soluble chromic salts, the amount of oxide requisite to give the red appearance depends greatly upon the acid with which it is combined. Thus, if equal portions of chromic oxide be dissolved in acetic and in sulphuric acids, it is very easy to arrange it so that, when viewed through glasses of equal capacity, the acetate appears red, and the sulphate green. If now to the red acetate a few drops of sulphuric acid be added, it passes through the neutral tint to the green colour; or if contrariwise, a little glacial acetic acid be added to the green sulphate, it assumes the reddish hue.

It is interesting to observe this change of colour by means of a prism. If a luminous object be viewed through any solution of a chromic salt, it exhibits two images, the one red, and the other green, fringed with blue. The relative intensity of colour of these two images differs with the amount of salt looked through, and with the character of the electro-negative element. On the addition of acetic acid, the red image becomes comparatively brighter and brighter, while the green image pales; and contrariwise, on the addition of hydrochloric or sulphuric acid, the green image becomes comparatively more and more distinct, while the red one fades. Again, if a solution of the acetate be seen through the sides of a wedge-shaped glass vessel, the stratum near the angle will appear green, that near the broad end red, while about a certain line neither colour will preponderate. On the addition of sulphuric acid this line advances towards the broad end, while acetic acid brings it again nearer the angle.

Ferrous Salts.—The mutual displacement of sulphuric and acetic acids may be also rendered visible by means of the protoxide of iron. If to a green solution of sulphate of iron a solution of acetate of potash be added, a brown colour is the result. If sulphuric acid

be added to this, the pale colour is more or less restored; if an addition of acetate of potash be then made, the brown reappears. This may be repeated many times with the same solution.*

Cobalt Salts.—The sulphocyanide of cobalt in an anhydrous condition, like the chloride, is blue; but, unlike that salt, it retains its blue colour when dissolved in a little water. As the solution is diluted, it gradually assumes the red tint which characterises solutions of the compounds of this metal. If very strong solutions, containing corresponding equivalents of chloride of cobalt and sulphocyanide of potassium, be mixed, a blue colour makes its appearance, showing the formation of sulphocyanide of cobalt. But that the double decomposition has not been complete, may be made evident by carefully diluting the blue mixture with water till it has become distinctly red, and dividing it into two parts. If to the one portion some of the very strong solution of sulphocyanide of potassium be added, the blue colour is restored; on the addition of more water, it disappears; and this may be repeated a number of times, until ten or twelve equivalents of sulphocyanide of potassium has been added to one of chloride of cobalt. If, inversely, to the other portion of the original mixture chloride of cobalt be added, that substance also produces a blue colour, which may be likewise caused to become red, or to reappear many times, by the successive addition of water or chloride of cobalt.

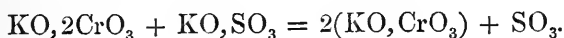
Chromates.—During the past year the “*Journal de Pharmacie et Chimie*”† has published an extract, in which Margueritte proves that “chromic acid can displace hydrochloric, nitric, and even sulphuric acids, and take away from them a part of the base to which they are united, whether that base be strong or weak.” We all know that these acids are capable of displacing chromic acid; indeed, the same investigator has shown that even boracic and carbonic acids will decompose bichromate of potash. By a method of observation almost identical with that adopted by myself, he found that the addition of such salts as chloride of potassium, or the nitrate or sulphate of potash or ammonia, to a solution of the red bichromate of potash, caused the production of yellow monochromate. Such experiments, he conceives, lend support to his view of “the partition of a base between the two acids, when any acid is added to any saline solution;” which is identical with the

* This experiment was suggested by a remark in Professor Miller’s Chapter on “Some Circumstances which Modify the Operations of Chemical Affinity,” in his “*Elements of Chemistry, Theoretical and Practical*,” vol. ii.

† *J. Pharm.* [3] xxvii. 21.

law of Berthollet, or rather is included in the more general expression.

One objection, however, may be taken to this conclusion from Margueritte's experiments. It may be contended that the salt added merely displaces the one equivalent of chromic acid in the bichromate of potash, and that, in fact, the reaction is according to the formula :



Indeed, this idea seems to have been in the mind of Schweizer, in a paper published a few months ago on these reactions of chromic acid.* The point seemed to admit of easy determination, for if the decomposition really take place in that manner, the production of the yellow colour will be perfect when single equivalents of the two salts are mixed, and no subsequent addition of sulphate of potash will lighten the tint. On trying the experiment it was found to be otherwise. The addition of one equivalent of sulphate of potash to one of bichromate of potash caused certainly a diminution of the red tint; but successive additions of the sulphate to the previous mixture caused the yellow to become more and more decided. Hence it may be concluded, that the mixture of single equivalents contains both bichromate and monochromate of potash, besides sulphuric acid and sulphate of potash, and possibly free chromic acid.

Copper Salts.—M. Alvaro Reynoso has recently published some "facts relating to the double decomposition of salts."† By taking advantage of the power of glucose to reduce the acetate of copper, he finds that when acetates of the alkalies, earths, or metals, are mixed with the nitrate or sulphate of copper, the acetate of that metal is produced. This is, so far, in accordance with the law of Berthollet; but whether the decomposition be complete or not does not appear from his experiments, though the action of mass is very evident in some of them. One remark, however, presents some difficulty. He observed that acetate of copper, mixed with ferric nitrate or sulphate, loses the property of being reduced by glucose. This I have repeated quantitatively. Solutions of acetate of copper and nitrate of iron were prepared of known strength; they were mixed together in certain proportions, with the addition of glucose, and boiled.

* J. pr. Chem. lxx. 173.

† Compt. rend. xli. 278.

| Salts mixed with glucose. | | | | | Result. |
|-----------------------------|---|---|-----------|----------------|----------------------------------|
| Acetate of copper | | | | | Immediate decomposition. |
| 3 eq. | " | " | + 1 eq. | ferric nitrate | Deposit after boiling. |
| 3 eq. | " | " | + 1·5 eq. | " " | Deposit after long boiling. |
| 3 eq. | " | " | + 2 eq. | " " | Deposit after very long boiling. |

From this it may be concluded that $3(\text{CuO}, \text{AcO}_3) + \text{Fe}_2\text{O}_3, 3\text{NO}_5$ do not become wholly $3(\text{CuO}, \text{NO}_5) + \text{Fe}_2\text{O}_3, 3\text{AcO}_3$. This also was confirmed by the colour: for the mixture of two equivalents of the ferric nitrate with three of acetate of copper was deeper in tint than when the salts were mixed in the proportions merely necessary for the above double decomposition.

This reaction, then, instead of militating against the conclusion illustrated in this paper, serves to support it.

In the "Comptes rendus" for last year, there also appear papers by Tissier* and Bineau,† narrating experiments confirmatory of the views arrived at by myself and other investigators; but they call for no further remark.

EVIDENCE FROM CIRCULAR POLARISATION.

Camphorates.—It was an early idea of mine that the effect of chemical affinity among substances in solution might be tested by means of circular polarisation; yet the evident intricacies of the subject deterred me from making any experiments: nor, indeed, did I see a case suited to my purposes. M. Bouchardat,‡ however, has announced that camphoric acid dissolved in alcohol causes a right-handed rotation; and that when it is saturated with a base, the rotation is considerably diminished, but is restored again on the supersaturation of the base by another acid. Yet, if I understand his experiments rightly, it appears that in the latter case the original amount of rotation is not quite obtained. Thus he gives the numbers:—

| | |
|---|--------|
| Camphoric acid | 12° R. |
| The same, saturated with soda | 7° R. |
| The same, supersaturated with hydrochloric acid | 11° R. |
| Camphoric acid | 22° R. |
| The same, saturated with ammonia | 12° R. |
| The same, supersaturated with hydrochloric acid | 21° R. |

* "On some Facts relating to Double Decomposition," p. 362.

† "On the Solubility of certain Metallic Oxides and Earthy Carbonates, and on some Reactions produced by their Solutions," p. 509.

‡ Compt. rend. xxviii. 319.

Are we wrong in deducing from these results that the hydrochloric acid did not completely decompose the alkaline camphorates first formed?

SALTS DISSOLVED IN ACIDS.

Sulphate of Baryta.—Within these last few months, no less than four papers have appeared, in which the solubility of sulphate of baryta in hydrochloric acid is discussed. Professor Rose,* Mr. Crace Calvert,† Dr. Noad,‡ and Messrs. Nicholson and D. Price,§ have shown by independent experiments, not only that sulphate of baryta is, to a certain extent, soluble in these acids, but that the amount dissolved is most materially diminished by the presence of an excess of baryta salt. Rose states that the solution of pure sulphate of baryta in either of the above-mentioned acids gives a small precipitate when treated with either chloride of barium or dilute sulphuric acid. He says, “It is a striking circumstance that the presence of the dissolved sulphate of baryta is indicated by both these reagents,” and he concludes that the salt in question “is less soluble in sulphuric acid and in chloride of barium than in hydrochloric acid and nitric acid.” Yet the great analytical chemist can scarcely offer this as a satisfactory explanation; for, in the experiment, the acid solvent still remains, capable, of course, of exerting its former power. Indeed, the next sentence shows the insufficiency of the reason; for Rose remarks that sulphate of baryta does not separate from the acid solution by means of water, although it is assuredly less soluble in water than in hydrochloric or nitric acids.

However, this “striking circumstance” is precisely what might be expected if the law of reciprocal decomposition, as quoted above, be true. If sulphate of baryta in excess be treated with an acid—say nitric—that portion which is brought into solution will suffer partial decomposition, and a solution will eventually result, containing as much sulphate of baryta as the free acid is capable of dissolving, and as much nitrate of baryta and sulphuric acid as is capable of counterbalancing the two other bodies. Such being the case, the addition of either sulphuric acid or baryta salt will disturb the equilibrium, with the production of fresh sulphate of baryta, which must precipitate, seeing that the acid solution was previously saturated.

Sulphate of Strontia.—Rose observed the same with sulphate of

* Pogg. Ann. xcv. 108.

† Proc. Roy. Soc. vii. 532.

‡ Chem. Soc. Qu. J. ix. 15.

§ Phil. Mag. 1856 [4], xi. 169.

strontia as he did with sulphate of baryta. Of course it is capable of the same explanation.

Sulphate of Lime.—On examining a solution of sulphate of lime in hydrochloric acid, Rose observed that a precipitate formed when it was treated with sulphuric acid, but not when it was treated with a solution of chloride of calcium. That this precipitation by sulphuric acid is incapable of the explanation offered by him in the case of sulphate of baryta, he shows by the observation that “a concentrated solution of sulphate of lime in water is *not* precipitated by sulphuric acid.” But the non-precipitation by chloride of calcium presented a difficulty to my explanation.

Two possible reasons suggested themselves to me, and, fortunately, each was capable of being put to the test of experiment. It might be that one equivalent of sulphate of lime is capable of being dissolved (or decomposed) by not more than one equivalent of hydrochloric acid. In that case, the formation of any amount of sulphate of lime from chloride of calcium would set free an equivalent amount of hydrochloric acid, which would keep it in solution. It was found, however, that one equivalent of sulphate of lime required three equivalents of hydrochloric acid (somewhat dilute) at the ordinary temperature to dissolve it.

The other supposition was that chloride of calcium might itself exert a solvent action on sulphate of lime; but this was found not to be the case.

The only supposition, then, that seemed possible, if my view were correct, was that such a small amount of additional sulphate of lime was formed that it was soluble in the water which was added at the same time as the chloride of calcium. This, happily, was also capable of being put to the proof by employing a very concentrated solution of the chloride. On doing so, a cloudiness at once appeared, which soon became a decided precipitate of crystallised sulphate of lime.

These reactions are all explicable on the supposition that when sulphate of lime is dissolved in hydrochloric acid, nearly (but not quite) all is converted into chloride of calcium.

Though sulphate of lime is not rendered more soluble in water by the presence of chloride of calcium, it does dissolve more freely when *other* chlorides are present. A. Vogel* has shown this in reference to chloride of ammonium and common salt: I have tried the experiment with four metallic chlorides—those of zinc, copper, iron, and chromium, and have found it to be the case with each.

* J. pr. Chem. xi. 196.

Now this is precisely what might be expected, supposing the two salts to suffer reciprocal decomposition, with the conversion of more or less of the sulphate of lime into the very soluble chloride. Vogel observes that when the solution in chloride of ammonium is evaporated to dryness, and heated to redness, pure sulphate of lime remains; and this has been employed as an argument against Berthollet's views: yet when we reflect how very volatile is the ammoniacal chloride, while the sulphate is not volatilised without decomposition, we shall see that no other final result could be obtained.

Sulphate of Lead.—Wackenroder* states that sulphate of lead dissolved in nitric acid is precipitable by sulphuric acid. I find that such a solution gives a precipitate also when treated with nitrate of lead.

This case is mentioned, because a statement of Wackenroder has been employed as an argument against the Berthollian hypothesis. The German chemist says that sulphuric acid, in large quantity, precipitates the sulphate of lead *completely*, notwithstanding the presence of the nitric acid. Yet, farther on in his paper, he proves that the said precipitation is *not* absolutely complete, and it is evident that, by employing the word "*vollständig*," he merely meant to say that the action was sufficiently perfect for ordinary analytical purposes.

Sulphate of Mercury.—Wackenroder also shows that the insoluble sulphate of mercury dissolved in nitric acid is precipitable by sulphuric acid.

Oxalate of Lime.—In order to vary these observations by experiments on other salts than sulphates, a saturated solution of oxalate of lime in dilute hydrochloric acid was prepared. On the addition of oxalic acid, a white precipitate after a while made its appearance; and on the addition of chloride of calcium to another portion, a precisely similar result ensued.

Chloride of Lead.—Dilute nitric acid was saturated with chloride of lead, and divided into two portions. To the one, hydrochloric acid was added, which caused an instantaneous precipitate; to the other, nitrate of lead was added, and, after some time, long crystals of chloride of lead formed.

Phosphate of Iron.—Hitherto the fact, that when a salt insoluble, or slightly soluble, in water, has been dissolved in an aqueous solution of any acid, the base divides itself in certain proportions between the two acids, has been deduced merely from the reactions

* Ann. Ch. Pharm. xli. 316.

of which such a solution is capable. It seemed desirable to prove this, if possible, by direct ocular demonstration. Phosphate of iron appeared to offer an opportunity of doing so. It is white in the solid state, but dissolves in hydrochloric acid with an orange colour. Now, if this colour be due to ferric chloride, we have a means of judging whether the whole of the iron be in that condition. Accordingly, some dilute hydrochloric acid was saturated with ferric phosphate. A portion was found to contain the same amount of colour as an aqueous solution of 0.067 grm. of ferric chloride; but the acid liquid itself consisted of 0.585 grm. of ferric phosphate dissolved in 0.477 grm. of real hydrochloric acid. Evidently, therefore, the whole of the iron was not in the state of chloride; indeed, supposing the ferric phosphate to have been of the usual composition, $2(\text{Fe}_2\text{O}_3)\cdot 3\text{PO}_5$, the amounts of iron in the two equi-tinted solutions were—

In the solution containing both phosphoric
and hydrochloric acids 0.164 grm. Fe.

In the solution of pure ferric chloride 0.023 „ „

Hence it would appear, that when ferric phosphate is dissolved in the smallest possible amount of hydrochloric acid, only one-seventh part is converted into the chloride.

It is here assumed that the ferric phosphate, which is white in its pure state, has no colour of its own when dissolved. In other ways, also, the above numbers may not be very exact; yet one thing is certainly proved,—that when phosphate of iron is dissolved in a minimum of hydrochloric acid, it is not wholly, or principally, converted into the chloride.

It may be expected that if a considerable amount of the iron still remain as phosphate, the addition of more hydrochloric acid will decompose more or less of this, and increase the colour. Such was found to be actually the case.

These experiments could not be advantageously performed by looking horizontally through the solution, for the golden tint of the ferric chloride is very little altered by dilution. A comparison, however, is easily made by looking perpendicularly through the solutions contained in glasses of uniform diameter.

The addition of phosphoric acid to the acid solution of ferric phosphate gave an immediate flocculent precipitate. I failed, however, to obtain a precipitate on the addition of ferric chloride. This is the first exception to the general inference that if a salt AB dissolve in an acid CD, the addition of either AD or CB will cause the production of more AB than the acid can keep in solu-

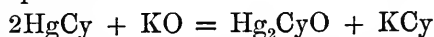
tion; yet when the peculiarity attending the saturating power of phosphoric acid is considered, it will probably present no great difficulty to the reception of that as a general law.

REPUTED EXCEPTIONS.

Beside the *primâ facie* difficulties already discussed, other reactions have been urged against the general conclusions adopted by me, and these claim a careful examination.

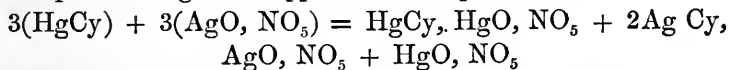
Cyanide of Mercury.—Reactions of an apparently anomalous character take place among mercury salts: thus, the cyanide affords two instances where an insoluble compound does not form, although, from the reciprocal decomposition of the compounds mixed together, it might be expected to make its appearance. When the cyanide of mercury is treated with potash in solution, the insoluble oxide does not precipitate; and when mixed with nitrate of silver it produces none of the insoluble cyanide of that metal.

The first of these apparent anomalies depends perhaps on the formation of the well-known oxycyanide of mercury, which is a ternary compound soluble in water. The annexed formula represents this decomposition:—



though such a mixture may contain, I apprehend, simultaneously all the four substances, besides the double cyanide of mercury and potassium.

As to the second anomaly, cyanide of mercury forms a soluble crystalline double salt with nitrate of silver, which has been analysed by Wöhler,* who assigns to it the composition $\text{AgO}, \text{NO}_5, 2\text{HgCy}, 4\text{HO}$. But were we to overlook this, the decomposition might be supposed to take place thus:—



all of which, beside the original salts, are soluble in water.

Boracic Acid.—The objections most frequently urged are founded on the behaviour of boracic acid. It is contended that this acid has no power to decompose sulphate of potash, and that borax is completely decomposed by an equivalent of sulphuric acid. I have already shown† that the non-alteration in colour of litmus does not prove this, but I have in vain sought for some property which would enable us to decide what actually does take place in the above-mentioned mixtures. Indications, however, have been ob-

* Pogg. Ann. i. 231.

† Phil. Trans. 1855, 220.

tained where boracic acid was mixed with another sulphate, and also where it was mixed with another potash salt; and in each of these cases it was found capable of effecting some decomposition.

The borate of quinine in solution, like the hydrochlorate, is non-fluorescent, or nearly so. If boracic acid be added to a neutral, and consequently non-fluorescent solution of sulphate of quinine, it immediately exhibits the beautiful surface blue, just as though a drop of hydrochloric acid had been added, and doubtless from the same cause—the formation of some bisulphate through the abstraction of some of the quinine by the other acid.* The addition of a very large quantity of boracic acid appeared to diminish the colour, and consequently to indicate the decomposition of the bisulphate; but I certainly never succeeded in destroying the fluorescence, as is easily done when the powerful hydracids are employed.

Three solutions were prepared—the first of boracic acid, the second of pure nitrate of potash, the third of a mixture of the two; and they were digested for some time with metallic copper, after which the solutions were tested with ammonia in excess. The first showed absolutely no blue, the second only a faint trace, while in the third the blue colour was very decided. From this it may be inferred that the boracic acid had displaced some of the nitric acid, which in its turn had attacked the copper. The quantity of copper dissolved must, however, have been exceedingly small.

It has also been objected that boracic acid occasions no precipitate in a solution of nitrate of lime, although borate of lime is an insoluble salt. Now there are said to be compounds of boracic acid and lime, which are not insoluble in water: and, moreover, the production of borate of lime from the nitrate must liberate an equivalent amount of nitric acid, which of course will exert its own solvent power. But while the non-precipitation of a borate is evidently inconclusive as to what really happens in the mixture, it appeared to me that metallic copper would also in this case furnish an indication. The experiment was accordingly tried as with the potash salt, and it was found that the neutral nitrate of lime had no action on copper, while the mixture of nitrate of lime and boracic acid produced a solution which was rendered blue by ammonia, and during the digestion a gelatinous substance formed in small quantity about the shreds of copper.

* See Stokes's paper, *Phil. Trans.* 1852, 542; also, 1855, 210.

It thus appears that boracic acid is able to displace other acids from their combinations, though but to a slight extent, in the cases just examined.

REGULAR PROGRESSIVE CHARACTER OF THE INFLUENCE OF MASS.

From the experiments detailed in the paper already referred to, I was led to the conclusion, that—"An alteration in the mass of any of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regular progressive ratio; sudden transitions only occurring where a substance is present, which is capable of combining with another in more than one proportion." Yet there is one experiment recorded which appears to offer an exception, and to indicate changes of ratio somewhat similar to those observed by Bunsen and by Debus, in cases where the resulting compounds were not capable of reacting. This experiment is where a solution of oxalate of lime in hydrochloric acid was precipitated by the addition of acetate of potash or soda. The table drawn out, and the curves projected from the experiments, show considerable irregularities; but as each experiment consists of six or eight separate observations, it was thought desirable to repeat the experiment, taking every precaution to ensure the observations being all made under the same circumstances.

Into each of ten glasses were poured 400 grain measures of a solution of oxalate of lime in hydrochloric acid. Different amounts of a solution of acetate of potash were mixed thoroughly with these, and the solutions were made up to the same bulk by the addition of water. After standing twenty-four hours, the resulting precipitates were washed the same number of times by suffusion and decantation; they were then boiled with pure water, and collected.

| Oxalate of lime in hydrochloric acid. 400 gr. meas. | Acetate of potash added. 50 gr. meas. | Oxalate of lime precipitated. 0·015 grm. |
|---|---|--|
| 400 " | 100 " | 0·049 " |
| 400 " | 150 " | 0·102 " |
| 400 " | 200 " | 0·136 " |
| 400 " | 250 " | 0·193 " |
| 400 " | 300 " | 0·278 " |
| 400 " | 350 " | 0·336 " |
| 400 " | 400 " | 0·350 " |
| 400 " | 500 " | 0·354 " |
| 400 " | 600 " | 0·354 " |

On the addition of potash to the filtrate from the last experiment of this series, a slight turbidity was produced, from the separation of oxalate of lime, showing that the whole of the hydrochloric acid had not even in that case been converted into chloride of potassium.

From the table it will be seen that a larger addition of acetate of potash caused a larger deposit of oxalate of lime, and that in a ratio which, though somewhat remarkable, was tolerably regular in its character. As it may be interesting to know the proportionate equivalents of the substances in each experiment, they are given in the annexed table. The initial 400 grain measures of acid solution contained 0.375 grm. of oxalate of lime, dissolved in 2.26 grms. of hydrochloric acid, nearly the proportion of 1 equiv. to 12; and each 100 grain measures of the acetate of potash solution contained 1.80 grm. of the anhydrous salt.

| Oxalate of lime. | Hydrochloric acid. | Acetate of potash. | Oxalate of lime deposited. |
|------------------------|-----------------------|--------------------------|----------------------------------|
| 1 equiv. | 12 equiv. | 1.75 equiv. | 0.04 equiv. |
| 1 „ | 12 „ | 3.5 „ | 0.12 „ |
| 1 „ | 12 „ | 5.25 „ | 0.27 „ |
| 1 „ | 12 „ | 7. „ | 0.36 „ |
| 1 „ | 12 „ | 8.75 „ | 0.51 „ |
| 1 „ | 12 „ | 10.5 „ | 0.74 „ |
| 1 „ | 12 „ | 12.25 „ | 0.90 „ |
| 1 „ | 12 „ | 14. „ | 0.93 „ |
| 1 „ | 12 „ | 17.5 „ | 0.95 „ |
| 1 „ | 12 „ | 21. „ | 0.95 „ |

The examination of these new substances, and of those reactions which appeared to be exceptional, tends therefore only to confirm the former conclusions. I propose to investigate, as they arise, any further objections founded on experiment.

REPORT OF THE COUNCIL

OF THE

CHEMICAL SOCIETY,

MARCH 31, 1856.

THE Council are glad to be able to congratulate the Society again upon its steady prosperity, as will appear from the following statement of the number of Fellows, and of the Accounts as reported by the Treasurer.

| | |
|--|-----|
| The total number of Fellows is | 256 |
| Deaths and resignations since the last Anniversary Meeting | 6 |
| Fellows admitted since last Anniversary | 9 |
| Increase | 3 |

Fellows deceased :—

Professor J. F. W. Johnston, M.A., F.R.S., Durham.

Professor J. E. Bowman, King's College, London.

Mr. W. Richardson, Denmark-hill.

James F. W. Johnston was born at Paisley in the year 1796. Part of his early childhood was spent in Manchester, whither his father for a time removed, but afterwards settled with his family at Kilmarnock. Young Johnston was at early age thrown upon his own resources, and, during the time that he was studying in the University of Glasgow, supported himself for some years by private tuition. In 1825, he took the charge of a proprietary school in Durham, and in the year 1830, married one of the daughters of Mr. Ridley, of Park End. Being now possessed of a competence which enabled him to follow his scientific tastes, he

shortly afterwards proceeded to Stockholm, with the view of studying chemistry in the laboratory of Berzelius.

In the year 1833, the University of Durham was opened, and the Readership of Chemistry and Mineralogy was conferred upon Mr. Johnston. He continued to hold this office during the remainder of his life; but for many years, excepting during term time, he resided in the neighbourhood of Edinburgh.

In 1843, he was appointed chemist to the Agricultural Society of Scotland. When that Society was dissolved, he left Edinburgh, and took up his abode at Durham, and it was here that he expired, on the 15th September, 1855, in the 59th year of his age.

Professor Johnston published several memoirs upon different purely chemical subjects. Amongst the best known of these, is his paper upon Paracyanogen; one upon the Vanadate of Lead; on a particular Hydrate of Sulphate of Lime; and besides these he published several other Mineralogical and Geological papers. The "Philosophical Transactions" for 1839-40, contain an elaborate series of researches by Professor Johnston on the resins. He also communicated to this Society, in 1842, a short paper upon the peculiar sugar contained in the manna of the Eucalyptus, which has since been more fully studied by Berthelot.

Professor Johnston took a warm interest in the earlier proceedings of the British Association, and contributed some valuable reports to its Transactions, particularly one upon the present state of chemistry, which appeared in the volume for the year 1832.

But it was as a clear expositor of Science that he was particularly distinguished. His most attractive work, and the one best known to the general reader, is that on the "Chemistry of Common Life," which exhibits his peculiar facility of imparting scientific truth, often of an abstruse kind, in a form acceptable to the non-scientific reader. It displays the extensive reading of the author, and the discriminative skill which characterized him, in no ordinary degree, in the choice and arrangement of his materials.

The most important works published by Professor Johnston are those which relate to Agricultural Chemistry. His lectures on Agricultural Chemistry and Geology contain a fund of sound and carefully digested information upon the subjects to which they relate, and the work constitutes the most complete systematic treatise upon those subjects, that has yet appeared. This work has passed through several editions; but one of his smaller works upon the same subject, the "Catechism" of Agricultural Chemistry, has attained a degree of popularity, which, for a scientific work, is

probably unexampled ; it has passed through thirty-three editions in this country, independent of numerous large editions in America, and it has been translated into various European languages.

Professor Johnston travelled widely both upon the Continent of Europe, and in America. He has left an agreeable account of part of his transatlantic experience, in his "Notes on North America." And he had just returned from an extensive journey in Central Europe, which he had undertaken, in connection with some geological inquiries in which he was engaged, when he was seized with a pulmonary attack, which terminated his life in a few days after his arrival at his own residence at Durham. Professor Johnston was one of the original members of the Chemical Society.

Mr. John Eddowes Bowman was also one of the original members of this Society. After a period of study in the laboratory of the late Professor Daniell, of King's College, he settled for a while at Manchester, where he availed himself of the facilities afforded him for becoming familiar with many important branches of manufacturing chemistry.

In the year 1845, he removed to London on the occasion of his appointment as Demonstrator of Chemistry in King's College, and on the creation of the Chair of Practical Chemistry in that Institution in 1851, he was selected as its first occupant. In the year 1846, Mr. Bowman contributed to the Transactions of the Society a paper on Tribasic Boracic Ether, but the feeble state of his health during the latter years of his life precluded him from active exertion in the laboratory. He is well known, however, as the author of two useful manuals, one on Practical Chemistry, the other on Medical Chemistry ; each of which has gone through two or three editions. Mr. Bowman possessed the art of interesting his pupils strongly in the subject which they were studying, and from the clearness and facility with which he imparted information was highly popular with his class.

During the last three years of his life, Mr. Bowman withdrew almost entirely from general society. The strength and excellence of his character was, therefore, comparatively little known ; but the few who shared his intimacy feel that with him they have been parted from a Christian friend, whose loss will not be easily replaced. Early in the month of February of the present year, he was attacked with influenza, which speedily reduced his already

enfeebled frame, and he expired on the 10th of February, in the 36th year of his age.

The following is a List of the Papers read before the Chemical Society between March 30, 1855, and March 31, 1856 :—

“On the Composition of the Waters of the Metropolis during the Autumn of 1854 :” by Dr. R. D. Thomson.

“On Platinised Charcoal :” by Dr. J. Stenhouse.

“On the Preparation of Strontium and Magnesium :” by Dr. Matthiessen.

“On the Preparation of Lithium :” by Professor Bunsen.

“On the Colour of Chloride of Copper in different States of Hydration :” by Dr. J. H. Gladstone.

“On the Proximate Constitution of Chemical Compounds :” by J. J. Griffin.

“A Few Notes on Barium :” by Dr. Matthiessen.

“On the Hydro-Electrical Currents Generated by Couples Formed of Single Metals :” by Richard Adie.

“On the Volatile Oil of *Ptychotis Ajowan* :” by R. Haines.

“On the Action of Light upon Chloride of Silver :” by F. Guthrie.

“On Azobenzole and Benzidine :” by Alfred Noble.

“On Insolinic Acid :” by Dr. A. W. Hofmann.

“Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre :” by F. A. Abel and C. L. Bloxam.

“On the Solubility of Sulphate of Baryta in Hydrochloric Acid :” by Dr. Noad.

“On a New Class of Alcohols :” by Dr. A. W. Hofmann.

“On the Source of the Water of the Deep Wells in the Chalk under London :” by Dugald Campbell.

“On the Action of Chloride of Cyanogen on Naphthalamine :” by William H. Perkin.

“On some new Colouring Matters, Derivatives of Dinitrobenzol, Dinitronaphthaline, &c. &c. :” by A. Church and W. H. Perkin.

The following Discourses have been delivered during the same period :—

“On the Maintenance of a Permanent Balance between the Animal and Vegetable Kingdoms, in a Medium of Fresh or Sea-water :” by R. Warington.

“On certain Processes recently proposed for the Decomposition of Fats by Water at High Temperatures:” by Dr. A. W. Williamson.

“On the Chemical Statistics of the Animal Body:” by Dr. J. H. Gilbert.

“On the Explosion at Gateshead in October 1854:” by Dr. G. D. Longstaff.

“On some points in the Practice of the Assay of Gold and Silver:” by Dr. W. A. Miller.

“On some new Bases containing Phosphorus:” by Dr. A. W. Hofmann.

“On some Laws of Chemical Combination:” by Dr. J. H. Gladstone.

ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY.

Cr.

| 1855. | 1856. | £ | s. | d. | By Payment of One Year's Rent to Polytechnic Institution..... | £ | s. | d. | |
|-----------|-----------|----|-----|-----|--|-----|-----|----|----|
| March 28. | March 29. | 31 | 15 | 10½ | " Ditto to H. Baillière for Publishing Journal... | 120 | 0 | 0 | |
| 1856. | " | | | | " Ditto of One Year's Salary to Editor of Journal | 131 | 18 | 6 | |
| March 29. | " | | | | " Ditto for Books and Periodical Publications... | 50 | 0 | 0 | |
| " | " | | | | " Ditto of One Year's Salary to the Librarian... | 61 | 15 | 0 | |
| " | " | | | | " Ditto to the Royal Society for their "Proceedings" sent to the Members of Chemical Society | 15 | 0 | 0 | |
| " | " | | | | " Ditto for Attendance and for Tea and Coffee... | 20 | 0 | 0 | |
| " | " | | | | " Ditto for Petty Cash, Postage Stamps, &c. ... | 41 | 15 | 10 | |
| " | " | | | | " Ditto to R. Ireland for a Book-case | 6 | 12 | 11 | |
| " | " | | | | " Ditto to Imperial Gas Company for Gas | 11 | 0 | 0 | |
| " | " | | | | " Ditto to Cavendish Society, Subscription 1856 | 1 | 10 | 0 | |
| " | " | | | | " Ditto for Coals and Wood | 1 | 1 | 0 | |
| " | " | | | | " Ditto to the Collector for Poundage | 1 | 10 | 0 | |
| " | " | | | | " Balance to his debit in next Account..... | 14 | 12 | 0 | |
| " | " | | | | | 94 | 14 | 6½ | |
| | | £ | 571 | 9 | 9½ | £ | 571 | 9 | 9½ |

London: 31st March, 1856.

ROBERT PORRETT, Treasurer.

Examined and found correct,

BENJAMIN H. PAUL, }
GEORGE SIMPSON, } Auditors.
HENRY M. NOAD, }

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

April 7, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

- “The American Journal of Science and Art:” from the Editors.
- “The Journal of the Franklin Institute:” from the Institute.
- “The Proceedings of the Royal Society:” from the Society.
- “The Pharmaceutical Journal:” from the Editor.
- “The Journal of the Society of Arts:” from the Society.
- “The Journal of the Photographic Society:” from the Society.
- “The Literary Gazette:” from the Publishers.
- “On the Constitution and Properties of Ozone:” by Thomas Andrews, M.D. From the Author.

The following gentlemen were elected Fellows of the Society:—

- Thomas J. Smith, Esq., Whitefriargate-street, Hull;
- George Jolly, Esq., 13, Curzon-street, May Fair;
- Henry Matthew Witt, Esq., Museum of Practical Geology, Jermyn-street;
- Thomas J. Dyke Acland, Esq., Sprydoncote, near Exeter.

The following papers were read:—

“Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre (second paper):” by F. A. Abel and C. L. Bloxam.

“On New Methods for the Estimation of Minute Quantities of Nitric Acid and Ammonia:” by J. Thomas Way.

April 21, 1856.

Dr. J. H. GILBERT in the Chair.

Thomas J. Smith, Esq., and A. H. Church, Esq., were admitted Fellows of the Society.

The following donations were announced :—

“ The Journal of the Society of Arts : ” from the Society.

“ The Journal of the Photographic Society : ” from the Society.

“ The Literary Gazette : ” from the Publishers.

James Allan, M.A., Ph.D., of 52, Hanover-street, Sheffield, was elected a Fellow of the Society.

Professor Abel delivered a discourse “ On Chemistry as applied to the Manufacturing Branches of the War Department.”

May 5, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced :—

“ The Literary Gazette : ” from the Publishers.

“ The Journal of the Society of Arts : ” from the Society.

“ The Pharmaceutical Journal : ” from the Editor.

“ The Journal of the Franklin Institute : ” from the Institute.

Alexander Harvey, Esq., of Glasgow, was elected a Fellow of the Society.

Dr. Warren De la Rue made a verbal communication upon “ Some Properties of the Metals of the Alkalies.”

The following papers were read :—

“ Note on a New Method of Making Ferricyanide of Potassium, and a Paracyanogen Compound : ” by Lyon Playfair, C.B., Ph.D., F.R.S.

“ On the Sulphovinates, and on Amylophosphoric Acid and the Amylophosphates : ” by Frederick Guthrie, Ph.D.

May 19, 1856.

Dr. WARREN DE LA RUE, Vice-President, in the Chair.

The following donations were announced :—

“The Literary Gazette :” from the Publishers.

“The Journal of the Society of Arts :” from the Society.

“The Proceedings of the Royal Society :” from the Society.

Samuel Clift, Esq., of Manchester, was elected a Fellow of the Society.

Mr. Alfred Harnett and Mr. John Attfield were elected Associates of the Society.

Dr. W. Odling made a verbal communication upon the “Distribution and General Characters of the Bibasic Organic Acids.”

Professor Abel remarked upon some “Circumstances connected with the origin of the late Explosions at Woolwich Arsenal.”

“Mr. H. M. Witt described some “Experiments showing the power of Filtering Media to remove the Dissolved Constituents of River Water.”

June 2, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced :—

“The Literary Gazette :” from the Publishers.

“The Journal of the Society of Arts :” from the Society.

“The Journal of the Photographic Society :” from the Society.

“The Proceedings of the Royal Society :” from the Society.

“The Pharmaceutical Journal :” from the Editor.

The following gentlemen were elected Fellows of the Society :—

William Kay, B.A., Stonyhurst, Whally, Lancashire ;

John Hamilton Clements, Esq., 4, Union-court, Old Broad-street.

The following papers were read :—

“On Lophine :” by A. Gössmann and E. Atkinson.

“On the Temperature of the Opposite Sides of a Bismuth Joint

while traversed by a Hydro-electrical Current:" by Richard Adie.—The author's experiments seem to show that the side of a medium at which electricity enters, is of a higher temperature than the side at which the electricity quits the medium. The differences observed were, however, very slight, seldom exceeding half a degree Fahrenheit.

"On the Analysis of a Meteoric Stone from the Desert of Atacama:" by Frederick Field.

"On the Decomposition by Heat of Native Oxichloride of Copper or Atacamite:" by Frederick Field.

June 18, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

- "The Quarterly Journal of the Geological Society:" from the Society.
- "The Journal of the Franklin Institute:" from the Institute.
- "The Literary Gazette:" from the Publishers.
- "The Journal of the Society of Arts:" from the Society.
- "On Electric Induction:" by Professor Faraday and Dr. Riess.

The following pamphlets and publications were presented by the Academy of Sciences at Munich:—

- "Denkrede auf Dr. Siber und Dr. Ohm, bei Dr. Lamont."
- "Zwei Reden: von F. Thiersch."
- "Ein Catalog der Veröffentlichungen, Reden und Verhandlungen der kaiserlichen Akademie."
- "Verhandlungen der mathematisch-physicalischen Klasse."
- "Gliederung der Bevölkerung Baierns: von Dr. Hermann."
- "Almanach der kaiserlichen Akademie der Wissenschaften."
- "Ursache der spontanen Bläuung einiger Pilze: von Schönbein, vom Verfasser."

Messrs. Piria, Schrötter, Strecker, and Wurtz, were elected Foreign Members of the Society.

August Dupré, Ph.D., of Deptford, was elected an Associate of the Society.

The following papers were read:—

“On Cadmium-Ethyle:” by J. A. Wanklyn.

“Description of a Self-acting Washing-Bottle:” by William Stephens Clark.

“On a Coal-gas Carbon and Nitric Acid Voltaic Battery:” by James L. and L. Wheeler.

“On the Analysis of the Iron used in English and Foreign Ordnance:” by F. A. Abel.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.

BY HENRY WATTS, B.A., F.C.S.

On the Constitution and Properties of Ozone.*

By Thomas Andrews, M.D., F.R.S., M.R.I.A.

AMONG the many interesting bodies which the researches of modern chemists have brought to light, few are more remarkable than the substance to which the name of Ozone has been given, whether we consider its many singular and anomalous properties, or its intimate relations with the most important and widely-diffused element in nature. For the first recognition of ozone and description of its properties, we are indebted to the sagacity of Schönbein, to whom the entire merit of the discovery unquestionably belongs. His earlier experiments were, however, chiefly directed to the elucidation of its properties, and of the conditions under which it is formed; but not being accompanied by quantitative determinations, they did not throw any clear light on its actual constitution. The subject has also attracted of late years the attention of several very distinguished physical and chemical inquirers, among whom I may particularly mention Marignac, De la Rive, Berzelius, Williamson, Fremy and Becquerel, and Baumert.

Schönbein has shown that a body having a peculiar and highly characteristic odour and very similar properties is formed under the three following conditions:—

1. When electrical sparks are passed through atmospheric air.
2. When pure water, or water holding certain acids or salts in solution, is decomposed by the voltaic current, the new substance appearing, along with the oxygen gas, at the positive pole.
3. When certain bodies, and particularly phosphorus, are slowly oxidised at common temperatures in atmospheric air.

Two distinct questions here arise for consideration. Is the same

* Phil. Trans. 1856, 1. 3.

substance produced under these different conditions, or has Schönbein included under the name of ozone substances having different compositions, although agreeing in some of their properties? And next, what is the composition of ozone; or, if there be more ozones than one, how are they respectively constituted?

The experiments of Williamson* indicated the production of water, when ozone obtained by electrolysis was decomposed by being passed over heated copper; and Baumert† obtained similar results when he passed a stream of electrolytic oxygen through a tube containing anhydrous phosphoric acid, which was heated at one point to redness. These experiments were not, however, adapted to yield quantitative results, but they led to the general conclusion that this variety of ozone is an oxide of hydrogen containing more oxygen than water. But from another and very important experiment, to which I shall have occasion hereafter very fully to refer, Baumert has concluded that it is a teroxide of hydrogen, HO_3 .

On the other hand, the experiments of De la Rive and of Fremy and Becquerel‡ have shown that pure and dry oxygen gas may be converted by the electrical spark into ozone.

I am not aware of any experiments on ozone obtained by the action of phosphorus on atmospheric air, which throw any distinct light on its constitution. Marignac passed a stream of this ozonised air through a solution of iodide of potassium, till the whole of the iodide was converted into iodate of potassa, and concluded that ozone produced in this way must be either oxygen in a peculiar state, or a peroxide of hydrogen.

According to the results, therefore, of the most recent investigations, it would appear—

That the substances comprehended under the name of ozone are not identical;

That the ozone obtained by the action of the electrical spark on oxygen gas is oxygen itself in an altered or allotropic state;

That the ozone obtained by the electrolytic decomposition of water is an oxide of hydrogen, having the formula HO_3 ; and

That the ozone obtained by the action of phosphorus on oxygen is either oxygen itself, or a compound of oxygen and hydrogen.§

The subject of ozone has at intervals engaged my attention during the last four or five years, and I was actually occupied with a series of experiments on the production of ozone by the electrical spark, when the appearance of Fremy and Becquerel's

* Memoirs of Chemical Society, ii. 395.

† Pogg. Ann. lxxxix. 39.

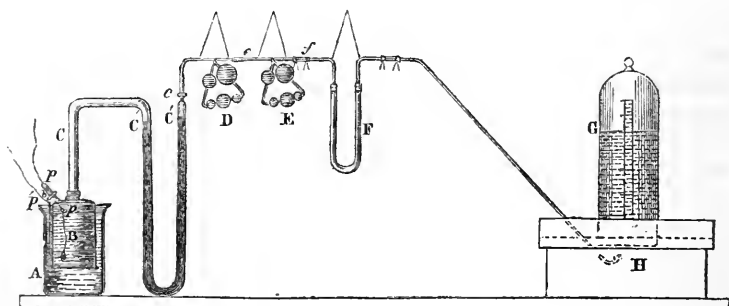
‡ Ann. Ch. Phys. [3] xxxv. 62.

§ For a very complete account of all that is known on this subject, see the article "Ozon" in the "Handwörterbuch der Chemie," v. 835 (Braunschweig, 1853).

able researches induced me for the moment to lay aside the inquiry. The publication of Baumert's memoir led me subsequently to resume it, as his results were not in accordance with those which I had previously arrived at. But the method proposed by that physicist to determine whether ozone is an oxide of hydrogen, or oxygen in an allotropic condition, appeared to be so well suited to the purpose, that on resuming the inquiry I considered it necessary, in the first instance, carefully to repeat his experiments. The results which I at first obtained were so far in accordance with those of Baumert, that they showed that the increase in weight of the apparatus was always more than the weight of the ozone, as deduced from its chemical action, but the relative proportion of these quantities was not in accordance with his results; nor, on repeating my own experiments, did they agree with one another. It was evident, therefore, that some disturbing cause existed which complicated the reaction, and, on further investigation, I not only found that such a cause did really exist, but succeeded in ascertaining its nature and the means of avoiding it. The experiments, on being now repeated, gave results very consistent with one another, and altogether at variance with the view that hydrogen is a constituent of ozone.

The apparatus which I employed was arranged as follows:—A is a vessel (Plate I. Fig. 1) of about two litres capacity, containing a mixture of one measure of pure and strong sulphuric acid and seven measures of distilled water. The cylinder B, which

FIG. 1.



is filled with a similar solution, is closed below with a diaphragm of bladder, so as to prevent effectually any mixture of the gases evolved at the two poles. A platina wire, *pp*, traverses and is fused into a short glass tube, fitted by grinding into the tubulated neck *b*: this wire terminates below in a bunch of fine platina wires, which form the positive pole of a voltaic arrangement. The negative pole is a platina plate, *p'*, immersed in the liquid of the outer vessel. The vessel A was placed in a larger vessel containing cold

water, to which ice was in some experiments added. This vessel has been omitted in the drawing for the sake of distinctness. $CC'C''$ is a continuous tube, united by fusion with the larger neck of B, and filled from C' to C'' with fragments of pumice, moistened with pure sulphuric acid. The length of the desiccating column was nearly one metre. D is a Liebig's apparatus, to the ends of which glass tubes were fused, which had previously been fitted by grinding, the one into the neck c of $CC'C''$, the other into a tube which was in like manner fused to a second Liebig's apparatus, E. The connections c and e were, therefore, formed by glass surfaces carefully ground. In my earlier experiments these connections were made by means of small and dry corks, which, on the whole, are more convenient than ground-glass joints, and are quite unobjectionable, as, when the surface is small and the cork dry, the amount of ozone destroyed by contact with the cork is wholly inappreciable. Caoutchouc connectors of any kind are altogether inadmissible; they are attacked with such energy by ozone, even when diluted with 1000 times its volume of other gases, that the tube becomes perforated in the course of a few minutes. The vessel D contained a solution of iodide of potassium acidulated with a little hydrochloric acid, and the vessel E concentrated sulphuric acid. The U-tube F, filled with pumice moistened with sulphuric acid, prevented any moisture from passing backwards into E. The oxygen evolved was collected in the graduated glass vessel G, inverted over water. The volume of the oxygen gas was determined only for the purpose of ascertaining its relation to the ozone produced.

The mixture of oxygen and ozone, having been perfectly desiccated in its passage through the long tube $CC'C''$, enters the vessel D, where the ozone is decomposed, iodine being set free and caustic potassa formed, which latter, combining with the free hydrochloric acid, forms chloride of potassium. If a neutral solution of iodide of potassium is employed, the reaction is more complicated; for, while the greater part of the iodine is set free as before, and dissolves in the excess of iodide of potassium, iodate of potassa and caustic potassa are at the same time formed. Whether the solution be taken in an acid or neutral state, the final result is in this respect always the same, that the active oxygen enters into a chemical combination in the vessel D, and increases the weight of the liquid contained in that vessel.

The increase in weight of the vessels D and E will give the entire weight of the ozone, whether that body be allotropic oxygen or an oxide of hydrogen. On the former supposition, the decomposition of the iodide of potassium will result in the substitution of oxygen for iodine, both remaining in D, while the sulphuric acid in E will retain the moisture which would otherwise be swept away by the

current of dry gas ; on the latter, ozone will become resolved into water and oxygen, both of which will be retained in the vessels D and E. Now by determining the amount of free iodine in the iodide of potassium solution at the end of the experiment, the amount of active oxygen by which it has been displaced may be easily calculated ; and on comparing this with the increase in weight of the vessels D and E, it will at once be seen whether ozone be a peroxide of hydrogen yielding water in its decomposition.

Two experiments of this kind were performed by Baumert : in the first, the increase in weight of the apparatus amounted to 0·0133 grm., and the weight of the oxygen, as calculated from the iodine set free, to 0·0081 grm. ; in the second, the same quantities were respectively 0·0149 grm. and 0·00989 grm. The iodide of potassium was employed in the state of a neutral solution, and the iodate of potassa was subsequently decomposed by the addition of a little hydrochloric acid.

It was from these results that Baumert inferred that the ozone which accompanies oxygen obtained by the electrolysis of water, is an oxide of hydrogen having the formula HO_3 ; and this conclusion, deduced from experiments which were devised with great skill and executed with care, has, in Germany at least, received very general assent.

Having, as already mentioned, found, on a repetition of these experiments, that a different expression resulted for the composition of ozone from every new trial, I instituted a diligent search into all the circumstances of the experiment, and at last succeeded in referring the irregularities to the presence of a small but appreciable quantity of carbonic acid, which, unless very great precautions be taken, is always present in electrolytic oxygen. When baryta-water was substituted for the solution of iodide of potassium in D, a precipitate of carbonate of baryta appeared in the course of a few minutes. With caustic potassa in the same vessel, the increase in weight for the same volume of oxygen gas was considerably greater than with the solution of iodide of potassium, and at the end of the experiment it was found that carbonate of potassa had been formed. Now as a small quantity of free potassa is always produced during the action of ozone on a neutral solution of iodide of potassium, it appeared not improbable that this would seize upon a portion of the carbonic acid just referred to, and thus the augmentation in the weight of the apparatus would depend upon two distinct causes,—the ozone reaction, and the absorption of carbonic acid. To prevent the occurrence of the latter, it was only necessary to acidulate the solution of iodide of potassium, so as to prevent the formation of free potassa, or to boil for some time the liquid subjected to electrolysis. The acidulation of the solution alone was found to be sufficient to prevent the carbonic

acid from being absorbed: for when this precaution was attended to, the results were the same, whether the electrolyte was boiled immediately before the commencement of the experiment or not. With this modification, the irregularities previously observed in different trials disappeared, and the simple and interesting result was obtained, that the increase in weight of the apparatus was exactly equal to the amount of oxygen deduced by calculation from the iodine set free.

I will now describe the chief precautions which I adopted to avoid, as far as possible, all sources of error in the following experiments, the delicacy of which will at once be apparent, if we consider that not more than 40 milligrammes of ozone are contained, under the most favourable circumstances, in 10 litres of electrolytic oxygen; and that it was necessary to have the arrangements so perfect, that this large quantity of gas (supposed to be free from ozone) should traverse the apparatus without producing any appreciable change in the united weight of the vessels D and E.

The solution of iodide of potassium employed in all the experiments had the same composition, although the quantity of ozone obtained in some cases was three times greater than in others. It consisted of 2 grms. of iodide of potassium dissolved in $22\frac{1}{2}$ grms. of a weak solution of hydrochloric acid, containing 2 per cent. of pure acid. As it is difficult to procure iodide of potassium entirely free from iodate of potassa, I always prepared, at the commencement of each experiment, two similar solutions, of which one was introduced into D, and the other preserved in a ground-stoppered vial, till the experiment was finished. The amount of free iodine in both was determined at the same time, and the difference taken to represent the exact quantity of iodine due to the ozone reaction. The correction for the iodate of potassa in the original solution, when reduced, rarely represented more than 0.001 gm. oxygen, but quantities of this magnitude must not be neglected in these experiments.

Previous to weighing the vessels D and E, one litre of atmospheric air, deprived of carbonic acid and carefully desiccated, was passed through the apparatus. The object of this precaution was to bring every part of the apparatus into the same state, at the beginning of the experiment, in which it would be at the end. The same volume of dry air was passed through the apparatus at the conclusion of each experiment.

It is rarely necessary in chemical investigations to apply a correction to the direct indications of the balance for changes in the temperature and pressure of the atmosphere, during the interval between two successive weighings. By preserving the apartment at a pretty uniform temperature, the corrections for thermometric changes may be confined within very narrow limits; but the

movements of the barometer are not under our control; and when, as in these experiments, a period of two and sometimes of three days elapsed between the first and second weighings, it occasionally happened that the change in the atmospheric pressure was considerable, and an appreciable error (amounting in some instances to nearly 0.002 grm.) would have occurred, if no correction had been applied.*

To ascertain how far the action of the apparatus might be relied on, one or two preliminary experiments were made, which gave very satisfactory results. The vessel D, containing pure water,—E, sulphuric acid,—and another Liebig's condenser also containing sulphuric acid, having been interposed between E and F, 3.5 litres of oxygen gas not containing ozone, followed by 1 litre of atmospheric air, were passed through the apparatus. The time occupied in the passage of the gas was about five hours. The vessel D lost 0.0311 grm., while E gained 0.0315 grm., the third vessel not sustaining any appreciable change of weight. If, therefore, D and E had been weighed together, the change of weight would have been only 0.0004 grm. In another experiment, in which a solution of strong caustic potassa was placed in D, the loss of D was 0.0175 grm., and the gain of E 0.0172 grm., the difference being less than one-third of a milligramme. Other experiments of the same kind, with different solutions in D, gave similar results. It is evident, therefore, that at the rate at which the gas traversed the apparatus, the whole of the moisture carried off from the liquid in D was retained by the sulphuric acid in E.

To determine whether a notable quantity of iodine would be carried over by the current of the gas from D to E, a solution of iodide of potassium containing a large quantity of free iodine was introduced into D, and a solution of pure iodide of potassium into E. After passing 4 litres of air through the apparatus, E was found to contain 0.0015 grm. iodine. This is equivalent to one-tenth of a milligramme of oxygen, and, from the large excess of iodine

* This correction was calculated as follows :—To the volume in cubic centimetres of the solution of iodide of potassium in D, and of sulphuric acid in E, was added the volume of the glass of which the vessels D and E were formed. From this was deducted the volume of the weights employed. Let v be the difference of the volumes so found in cubic centimetres; p and p' , the atmospheric pressures in English inches at the first and second weighings; t and t' , the corresponding temperatures in Centigrade degrees; x , the weight in grammes of a volume of air equal to v , measured under the pressure p , and at the temperature t ; x' , the weight of the same volume of air at p' and t' . Then, since 1 cub. cent. air at 0° , and under a pressure of 29.92 inches, weighs 0.00129 grm.,

$$x' - x = v \left(\frac{1}{1 + 0.00367 t'} \cdot \frac{p'}{29.92} - \frac{1}{1 + 0.00367 t} \cdot \frac{p}{29.92} \right) \cdot 0.00129.$$

The value of $x' - x$ is to be added to, or subtracted from, the increase of weight, as found by direct experiment, according as it is a positive or negative quantity.

in the first solution, must be a greater quantity than could have been carried over in any of the subsequent experiments, although in some of them larger volumes of gas were passed through the apparatus.

The free iodine was determined according to the very delicate method first, I believe, proposed by Bunsen. A dilute solution of sulphurous acid was prepared, and its strength determined, immediately before analysing the liquid in D, by ascertaining how many measures of it were required to destroy a known weight of free iodine in a solution of iodide of potassium. A corresponding experiment was made with the solution in D, from which the quantity of free iodine in it was deduced by a very simple calculation.

I. 10.2 litres of electrolytic oxygen containing ozone were passed through the apparatus at the rate of about three-quarters of a litre per hour. At the first weighing, the barometer was 29.85 in., and the thermometer $5^{\circ}9$ C.; at the second weighing, the barometer was 29.98 in., and the thermometer $5^{\circ}3$. The value of v (see preceding note) was 47 cub. cent. The gain in weight of the double apparatus D and E was 0.0375 gm., which gives, when corrected for atmospheric changes, for the true gain, 0.0379 gm. The free iodine in the solution contained in D was neutralised by 112.7 measures of a dilute solution of sulphurous acid. The other solution of iodide of potassium, which had been prepared at the same time as the first, and to which the same amount of acid had been added, required 0.8 measure of the same solution of sulphurous acid for neutralisation. Hence the iodine eliminated by the action of the ozone was equivalent to 111.9 measures. Next, 0.5341 gm. pure iodine was added, together with 2 grms. of iodide of potassium, to a few drops of water, and when both were dissolved, the solution was diluted till it occupied exactly 100 cub. cent. From the mean of two experiments which closely agreed with one another, it appeared that 100 measures of the solution of sulphurous acid neutralised 95.96 cub. cent. of this solution, and hence 1 measure of the former corresponded to 0.00512 gm. iodine. From these data it follows, by an easy calculation, that the iodine disengaged by the ozone amounted to 0.609 gm., and the equivalent of oxygen to 0.0386 gm.

II. 2.72 litres of electrolytic oxygen were passed through the apparatus at the same rate as before. At first weighing, barometer 29.60 in., thermometer $5^{\circ}8$ C.; at second weighing, barometer 29.60 in., thermometer $6^{\circ}0$ C. Gain of weight of D and E 0.0107 gm.; corrected, 0.0107 gm. The free iodine in D, after deducting the iodine due to the small quantity of iodate of potassa in the original solution, was neutralised by 30.23 measures of a solution of sulphurous acid, of which, as ascertained by direct ex-

periment made at the time, 1 measure neutralised 0·00521 gm. free iodine. Hence the oxygen due to the displacement of iodine was 0·0100 gm.

III. 2·86 litres of the same gas as in the preceding experiments were passed through the apparatus. At first weighing, barometer 30·06 in., thermometer 6°·6 C.; at second weighing, barometer 30·20 in., thermometer 6°·1 C. Gain of weight of D and E 0·0152 gm.; corrected, 0·0154 gm. The free iodine in D, corrected as before, was neutralised by 41·52 measures of a solution of sulphurous acid, of which 1 measure neutralised 0·00525 gm. iodine: hence the weight of oxygen, as deduced from the weight of iodine set free, was 0·0138 gm.

IV. 6·45 litres of electrolytic oxygen were passed through the apparatus. At first weighing, barometer 29·96 in., thermometer 6°·8 C.; at second weighing, barometer 29·29 in., thermometer 7°·8 C. Gain of weight of D and E 0·0303 gm.; corrected, 0·0288 gm. The free iodine in D was neutralised by 100·4 measures of a solution of sulphurous acid, of which 1 measure neutralised 0·00441 gm. iodine: hence the weight of oxygen deduced in this way was 0·0281 gm.

V. 6·8 litres of electrolytic oxygen passed. At first weighing, barometer 30·53 in., thermometer 9°·8 C.; at second weighing, barometer 30·44 in., thermometer 10°·4 C. Gain of weight of D and E 0·0254; corrected, 0·0251 gm. The free iodine in D neutralised 107·9 measures of a solution of sulphurous acid, of which 1 measure was equivalent to 0·00358 gm. iodine: hence the weight of oxygen deduced from the iodine set free was 0·0273 gm.

Collecting these results, and adding them together, so as to obtain the mean of the whole, we have

| Ozone deduced from the increase in weight of the apparatus. | Ozone deduced from the iodine liberated. |
|--|---|
| I. 0·0379 gm. | 0·0386 gm. |
| II. 0·0107 gm. | 0·0100 gm. |
| III. 0·0154 gm. | 0·0138 gm. |
| IV. 0·0288 gm. | 0·0281 gm. |
| V. 0·0251 gm. | 0·0273 gm. |
| ----- | ----- |
| 0·1179 gm. | 0·1178 gm. |

The agreement is complete, and proves unequivocally that water is not a product of the decomposition of ozone, which therefore does not contain hydrogen as a constituent. If its composition were HO_3 , the apparatus would have increased 0·1841 gm. in weight, instead of 0·1179 gm.

The amount of ozone formed in these experiments was tolerably

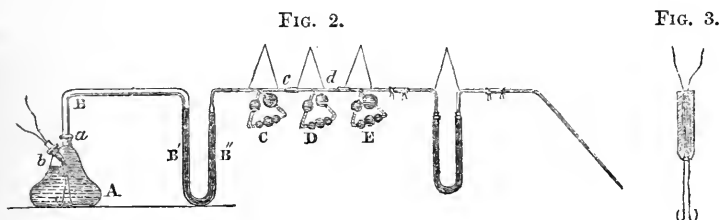
uniform. For 1 litre of oxygen the following weights of ozone were obtained :—

| | | |
|-------|--------|-------|
| I. | 0·0038 | gram. |
| II. | 0·0037 | gram. |
| III. | 0·0046 | gram. |
| IV. | 0·0043 | gram. |
| V. | 0·0040 | gram. |
| <hr/> | | |

Mean . . 0·0041 gram.

In the arrangement above described, the oxygen gas derived from the electrolytic decomposition of water was therefore accompanied by about $\frac{1}{350}$ th of its weight of ozone.

In order to remove every possible doubt from these results, I fitted up an apparatus from every part of which organic substances were excluded. No diaphragm was used, and all the connexions were made either by fusing the ends of the connecting tubes together, or by means of ground-glass joints. The arrangement is represented in Fig. 2. Two platina wires (Fig. 3) were fused into the end of a glass tube, which was fitted by grinding to the tubulated neck *b* of the vessel A. The tube BB'B'' was connected at *a*



with the vessel A by a ground joint, and with *c* by fusion. It contained pumice moistened with sulphuric acid. The vessel C was also filled with sulphuric acid, and was connected by a ground glass joint with the iodide of potassium vessel D. The vessel E contained, as before, sulphuric acid. In this experiment, both the hydrogen and the oxygen traversed the apparatus, the accuracy of which was thus exposed to a very severe test.

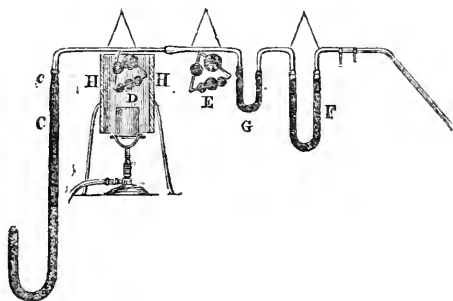
Twenty-two litres of the mixed gases were passed through the apparatus. The gain in weight of D and E was 0·0135 gm., the respective heights of the barometer at the first and second weighings having been 28·96 in. and 29·57 in., and the temperatures 11°·1 and 10°·0. The correction for change of pressure and temperature is therefore +0·0014 gm., and the true gain 0·0149 gm. The free iodine in D, due to the action of the ozone, neutralised 62·65 measures of a solution of sulphurous acid, of which 1 mea-

sure corresponded to 0.00373 grm. iodine. The weight of ozone deduced from the iodine set free is therefore 0.0148 grm.

The identity of these results is very satisfactory, when it is considered that this small weight of ozone was separated from 22 litres, or nearly five gallon measures of the mixed gases. The relative quantity of ozone to the amount of water decomposed is less than in the former experiments, arising perhaps partly from a single platina wire having been in this case employed as the positive pole. In this experiment, great care was taken to exclude both carbonic acid and nitrogen from the electrolyte.

My next object was to determine, by careful quantitative experiments, whether water is really formed, as Williamson and Baumert have stated, when ozone is decomposed by heat. For this purpose, the same general arrangement was employed as in the first series of these experiments; but the first Liebig's apparatus D, instead of being filled with a solution of iodide of potassium, was now empty, and placed in the upper part of a metallic cylinder (Fig. 4, HH), where it was raised to a temperature of about

FIG. 4.



400° C., by a current of heated air from a Leslie's burner. To the sulphuric acid apparatus E was permanently attached, and weighed along with it, a small U-tube G, containing anhydrous phosphoric acid, so as to secure the condensation of the last trace of aqueous vapour, if any were present. The oxygen gas was collected and measured as in the former experiments.

Two experiments were made. In the first, 6.8 litres of oxygen containing 0.027 grm. ozone were passed through the apparatus; in the second, 9.6 litres containing 0.038 grm. ozone. The compound sulphuric and phosphoric acid apparatus was found, all corrections having been made, to have increased, in the one case one-third, and in the other case one-half of a milligramme in weight. Such quantities can only be referred to the unavoidable errors of experiment. If ozone were a compound body having the constitu-

tion HO_3 , the apparatus would have gained in the first experiment 10, and in the second 14 milligrammes.

That ozone cannot contain nitrogen will appear from the following experiment. Two platina wires were hermetically sealed into the bottom of a small flask, into which water, containing a little sulphuric acid, was introduced, and made to boil rapidly for some time. While the water was in a state of ebullition, the wires were connected with the poles of a voltaic arrangement, so as to disengage the mixed gases along with the vapour of water. So long as the ebullition continued, no ozone made its appearance; but on allowing the liquid gradually to cool, without arresting the current, its presence soon became manifest from its odour and action on iodide of potassium paper. The ebullition and the current of the mixed gases must have rendered the presence of nitrogen here impossible.

One question still remains to be answered. Does ozone, besides oxygen, contain any other constituent which is not absorbable by any of the reagents employed? Although the gas which escaped from the apparatus, after the separation of the ozone, appeared to be pure oxygen, yet it would be rash to assert that it might not have contained some unknown body amounting to $\frac{1}{1000}$ th of its weight, and having no very salient properties. This question appeared to me to admit of solution in another way. It will be seen, in a subsequent part of this paper, that there can be no doubt of the formation of ozone from pure and dry oxygen by the action of the electrical spark; and nothing is easier than to convert the whole of a given volume of oxygen into ozone in presence of a solution of iodide of potassium. The next step in the inquiry was, therefore, to ascertain whether ozone derived from electrolysis, from the action of the electrical spark, and from the oxidation of phosphorus, exhibited a perfect identity in all its properties.

One of the most remarkable properties of ozone is its destruction by heat, or rather its conversion by heat into ordinary oxygen. To ascertain the temperature at which this change occurs, the vessel D, Fig. 4, was placed in a bath of mercury, and the gas examined as it escaped, without previously passing it through the rest of the apparatus. On heating the mercurial bath, the amount of ozone, as determined by its action on iodide of potassium paper,* did not notably diminish till the temperature attained 230°C . It still continued, however, very intense till the thermometer rose to 235° . Between that point and 240° , the ozone reactions entirely disap-

* Bibulous paper which has been dipped into a solution of iodide of potassium of moderate strength, and afterwards allowed to dry, but still retaining its hygrometric moisture, is the most convenient test of ozone. If it be exposed to a continuous current of dry air, it should be removed from time to time, and its hygrometric moisture restored.

peared, when the ozone was in a very dilute state; but when more concentrated, slight traces of ozone could still be discovered, which no doubt would have also disappeared if the current of gas had been passed very slowly. Time is, in fact, an element in this action. Even at the temperature of 100°C . ozone is slowly destroyed. Two similar tubes were filled at the same time, and by the same process, with ozone diluted as usual with oxygen, and afterwards hermetically sealed. One of these tubes was maintained for three hours in a vapour bath at 100°C ., the other was not exposed to heat. On examining both tubes at the end of the time, it was found that the ozone in the tube which had been exposed to heat was perceptibly less than in the other. I have no doubt that, even at the common temperature of the air, ozone preserved in an hermetically sealed glass tube would gradually change into common oxygen. I made an experiment of this kind two or three years ago, which resulted in the disappearance of the ozone; but I do not remember the source from which the ozone was derived, nor what precautions were taken to dry the gas.

On the other hand, ozone brought directly into contact with the vapour of water at the boiling point is instantly destroyed.

To obtain a continuous stream of ozone from the action of the electrical spark, a current of pure oxygen gas, obtained from the decomposition of the chlorate of potassa, and purified and dried by passing through tubes containing hydrate of potassa and sulphuric acid, was exposed to a rapid succession of electrical sparks. To obtain a sufficient stream of electricity, an electrical machine, firmly screwed down to the floor of the apartment, was connected by a belt with a heavy cast-iron wheel, 40 inches in diameter, contained in a frame which was also firmly secured to the floor. By this arrangement, the machine could be worked for any length of time continuously, the plate performing about 360 revolutions per minute. It was of course necessary to apply very frequently a hand rubber covered with amalgam to the plate, and it required the co-operation of three persons to permit the work to be easily performed. On passing the gas through the apparatus at nearly the same rate as in the experiments already described, an abundant stream of ozone was obtained, which enabled me to institute a very exact comparison between its properties and those of ozone obtained by electrolysis.

When heated in the mercurial bath, ozone prepared in this way was rapidly destroyed at the temperature of 237°C ., which is the same temperature at which electrolytic ozone was also destroyed. The vapour of boiling water, in like manner, caused all the ozone reactions to disappear.

The action of water at common temperatures and of alkaline solutions upon ozone is very remarkable. It is commonly stated

that caustic potassa absorbs ozone, but that pure water, and solutions of lime, baryta, and ammonia, have no action upon it. This statement is far from being accurate. Pure water does not absorb ozone, and a stream of air containing ozone may be passed for any length of time through water without producing any change in the properties of the water. I have also preserved ozone for several days in a stoppered vial containing a little distilled water, and, although the vessel was agitated from time to time, the ozone did not disappear. On the other hand, pure water has the property of destroying a small quantity of ozone. If ozone, obtained by the electrolysis of water, or by the action of the electrical spark, or by means of phosphorus, be largely diluted with atmospheric air, it will entirely disappear, if an attempt be made to collect it in a jar inverted over water. The following experiment is more precise:—A flask provided with a ground glass stopper, of the capacity of half a litre, was filled with equal volumes of water and atmospheric air, and inverted in the pneumatic trough. The ozone in a single bubble of electrolytic oxygen, passed quietly through the water into this volume of air, could easily be detected; but on agitating the water briskly, even four or five bubbles were deprived of their ozone. The same gas, agitated with twice its volume of lime-water, or one-third of its volume of baryta-water, also ceased to exhibit the reactions of ozone. In like manner, the action of caustic potassa is also limited. A strong solution of that alkali in a Liebig's apparatus deprived one litre of electrolytic oxygen of its ozone, after which the ozone passed freely through it. These phenomena are singular and characteristic, and are the same with ozone, from whatever source it is derived.

Peroxide of manganese destroys ozone, affording an interesting example of what is commonly called catalytic action. The oxide of manganese does not increase in weight, nor is water formed. Ozone from the three sources gives the same results.

The odour of ozone, from whatever source derived, is the same. The same remark applies to its property of bleaching, without producing at first an acid reaction.

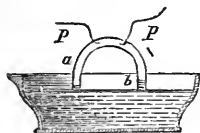
Iodide of potassium is decomposed, with the formation of iodate of potassa; and oxidable substances in solution, as the protosulphate of iron, are raised to a higher state of oxidation by all the varieties of ozone.

It would not be difficult to extend this comparison, but enough has been shown, I conceive, to establish the absolute identity in properties of ozone, in whatever way it may be prepared. Any difference which, on a superficial examination, may appear to exist, will be found on further inquiry to arise from the ozone being in a more or less dilute state.

That ozone is formed by the action of the electrical spark on

perfectly dry oxygen, is placed beyond all doubt by the following experiment:—The curved tube *a*, Fig. 5, having two platina wires, *pp'*, hermetically sealed into it, was inverted over mercury and carefully filled with pure oxygen, after which a little sulphuric acid was introduced into one end (*b*). The whole was allowed to remain for twenty-four hours, when the oxygen was considered to be perfectly dry. Electrical sparks were now passed for some time between the platina wires, after which a solution of iodide of potassium was introduced into the other end of

FIG. 5.



the tube. It became immediately coloured from the formation of free iodine, and the colour continued slowly to increase as the ozone was gradually absorbed.

Again, a solution of iodide of potassium may be made to absorb the whole of the oxygen in a narrow tube, by the passage of electrical sparks. This experiment has been described by Fremy and Becquerel, and I have myself repeatedly verified its accuracy. With a thermometer tube 2 inches long, the whole of the oxygen may be made to disappear in the course of one minute. The solution becomes always red from the decomposition of the iodide of potassium.

We have already seen that neither hydrogen nor nitrogen can be constituents of ozone, whether it be obtained from electrolysis, or from the action of the electrical spark on oxygen; and further, that all the supposed varieties of ozone exhibit in all respects identical properties.

Connecting all these facts together, it clearly follows —

That no gaseous compound having the composition HO_3 is formed during the electrolysis of water; and

That ozone, from whatever source derived, is one and the same body, having identical properties and the same constitution, and is not a compound body, but oxygen in an altered or allotropic condition.

On the Formation and Preparation of Formic Acid.

By M. Berthelot.

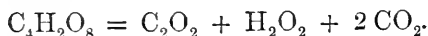
I. *Formation from Carbonic Oxide.**—The relation of carbonic oxide to formic acid is, in a certain sense, the same as that of olefiant gas to alcohol:



* Compt. rend. xli. 955; Ann. Pharm. xcvii. 135.

alcohol heated with strong sulphuric acid yields olefiant gas; and formic acid similarly treated yields carbonic oxide. Guided by these considerations, Berthelot endeavoured to prepare formic acid from carbonic oxide by a process analogous to that by which he had previously formed alcohol from olefiant gas.* The mode of proceeding adopted was to expose caustic potash to the action of carbonic oxide at a high temperature. 10 grammes of slightly-moistened hydrate of potash are introduced into 4 flasks of about half a litre in capacity; and the flasks filled with carbonic oxide, then sealed, and heated for 70 hours in the water-bath. On subsequently opening the flasks under mercury, the mercury fills them completely, showing that all the carbonic oxide has been absorbed; and on dissolving the contents of the flasks in water, supersaturating with sulphuric acid, and distilling, a distillate is obtained containing dilute formic acid.

II. *Preparation from Oxalic Acid.*†—Gay-Lussac showed that formic acid is produced in the decomposition of oxalic acid by heat, its formation resulting from the union of carbonic oxide and water in the nascent state:

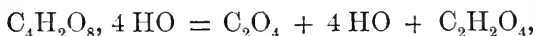


The quantity of formic acid thus obtained is, however, very small. But Berthelot has lately found that the whole of the carbonic oxide liberated by the decomposition of the oxalic acid may be made available for the production of formic acid, if the oxalic acid be mixed with glycerine, which appears in this case to act merely by contact. A mixture of 1 kilogramme of commercial oxalic acid, 1 kilogramme of syrupy glycerine, and 100 to 200 grammes of water, is introduced into a retort of 2 litres capacity, and gently heated, the temperature not being allowed to rise much above 100° C. Carbonic acid is then evolved with brisk effervescence, and in 12 to 15 hours, the whole of the oxalic acid is decomposed, half of its carbon being eliminated in the form of carbonic acid. A small quantity of water containing formic acid distils over, and the residue in the retort consists of glycerine containing nearly all the formic acid in solution. To separate the formic acid, half a litre of water is poured into the retort, and the liquid continuously distilled, the water being renewed as it evaporates, till about six or seven litres of liquid have passed over, containing in fact nearly the whole of the formic acid. The residual glycerine may be used in the same manner to convert fresh quantities of oxalic acid into formic. 3 kilogrammes of oxalic

* See Chem. Soc. Qu. J. viii. 148.

† Compt. rend. xlii. 447; Ann. Pharm. xcvi. 139.

acid yielded by this process 1.05 kil. formic acid. According to the equation:



the quantity should be 1.09 kil. The formic acid thus prepared is quite pure, and free from oxalic acid.

It is important that the decomposition of the oxalic acid be not too much hurried. If the temperature of the contents of the retort rise too high, a more rapid evolution of carbonic acid takes place at first; ceasing, however, after a while. The temperature then quickly rises to 190° — 200° , and a new evolution of gas commences, consisting of carbonic oxide. The liquid which distils over under these circumstances contains of course much less formic acid than would be obtained from the same quantity of oxalic acid, if slowly decomposed. This evolution of carbonic oxide proceeds from the decomposition of the formic acid dissolved in the glycerine (like ammonia in water). Pure formic acid also, when heated to 200° — 250° for some hours in closed vessels, is for the most part resolved into water and carbonic oxide gas. To obtain carbonic oxide from oxalic acid, Berthelot heats the oxalic acid mixed with glycerine; and collects separately the carbonic oxide which is evolved, when the heating is continued after the evolution of carbonic acid has ceased.

Chemical Notices.*

By H. Limpricht.

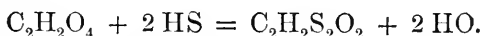
1. *Thioformic Acid*, $\text{C}_2\text{H}_2 \left\{ \begin{array}{l} \text{S}_2 \\ \text{O}_2 \end{array} \right.$.—When dry sulphuretted hydrogen gas is passed over formiate of lead at a temperature above 100° , for the purpose of preparing formic acid, the resulting acid has a disagreeable alliaceous odour, and not unfrequently small needle-shaped crystals separate from it. These crystals are obtained in greatest quantity when the decomposition of the salt is performed in a tubulated retort, which during the operation is heated to 200° — 300° by placing hot coals under it. The formic acid sometimes solidifies after a while in the receiver from separa-

* Ann. Pharm., xcvi 363.

tion of these crystals, and the liquid filtered from them yields after distillation a nearly equal quantity of the same product. If the crystals, after washing with cold water and drying over sulphuric acid, are not quite colourless, they may be recrystallised from alcohol; but the quantity of alcohol required for the purpose is very large. The product obtained from a pound of formiate of lead amounts to only a few grammes.

The amount of sulphur in the crystals was found by analysis to be 51.2 and 52.5 per cent. The formula $C_2H_2S_2O_2$ requires 51.6.

The formation of thioformic from formic acid may be represented by the equation,



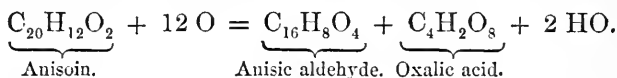
Thioformic acid crystallises from formic acid, or from boiling alcohol, in slender needles, melts at about 120° , and sublimes, even at a low temperature, in small transparent crystals. It has a faint alliaceous odour, is insoluble in water, dissolves with tolerable facility in alcohol and ether at the boiling heat, but scarcely at all in the cold; a portion of it volatilises, together with the alcohol-vapours.

Strong sulphuric acid dissolves thioformic acid at a gentle heat, with evolution of sulphurous acid and separation of sulphur; strong hydrochloric acid has no action upon it, even at a boiling heat; nitric acid decomposes it readily when heated, oxidising the sulphur to sulphuric acid; strong acetic acid dissolves it in small quantity at a boiling heat, but deposits it again on cooling. When thioformic acid is heated with dilute sulphuric acid and peroxide of lead, the latter assumes a lighter colour; with chromate of potash and dilute sulphuric acid, it forms sesquioxide of chromium. Fused with hydrate of potash, it forms a reddish-yellow mass, which, when treated with dilute sulphuric acid, gives off sulphuretted hydrogen and an odour of garlic. Solution of potash dissolves it but sparingly, even at the boiling heat; and the solution treated with acids gives off traces of sulphuretted hydrogen. Thioformic acid is not soluble in sulphide of ammonium, either in the cold or at a boiling heat.

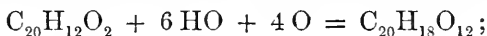
The alcoholic solution of thioformic acid has no reaction upon litmus; it is not altered by sesquichloride of iron; forms with acetate of lead a yellowish precipitate, which turns black when heated with the liquid; with nitrate of silver it yields an amorphous precipitate, which is white at first, but soon turns black, and dissolves partially in hot water, with separation of metallic silver or sulphide of silver. In consequence of its great proneness to decomposition, the silver-compound could not be obtained in a form adapted for analysis.

2. *Anisoic Acid*, $C_{20}H_{18}O_{12}$.

It is generally supposed that when oil of aniseed is acted upon by nitric acid, anisic aldehyde or anisylous acid and oxalic acid are formed in the first instance, according to the equation



The following experiments, however, render it probable that the first product of the action is a new acid,—anisoic acid :



and that this acid, when subjected to the further action of heat, yields anisic aldehyde and oxalic acid.

When oil of star-aniseed is heated with nitric acid of sp. gr. 1.2 till it sinks to the bottom, and then shaken up with a warm solution of bisulphite of soda, the aqueous solution yields on cooling, not sulphite of anisic aldehyde and sodium, but a soda-salt composed of $C_{20}H_{17}NaO_{12}$, viz., anisoate of soda. The acid of this salt has hitherto been obtained only from oil of star-aniseed; but it would doubtless be also produced from the other oils which contain anisoïn (viz., oil of aniseed, fennel, and taragon).

Anisoic acid, when separated from its silver or barium-salt by hydrochloric or sulphuric acid, crystallises by evaporation of its aqueous solution, in small laminae; but a concentrated solution left for some time in contact with the air deposits tolerably thick tables. The acid dissolves very readily in water, alcohol, and ether, and is therefore difficult to obtain in good crystals; it has a strong acid reaction, and melts at about $120^{\circ}C$. Heated on platinum-foil, it turns brown, gives off empyreumatic vapours having the odour of anisic aldehyde, and finally burns with a luminous flame. It cannot be sublimed without decomposition, even by careful heating.

A solution of the silver-salt, mixed with hydrochloric acid, having been accidentally left over the fire, together with the precipitated chloride of silver, till it had gone to dryness, a sublimate of white needles was found to have collected on the chloride of silver: these needles had the appearance of anisic acid, and the analysis of their silver-salt showed that they really consisted of that acid. An attempt to obtain anisic acid by heating free anisoic acid moistened with sulphuric or hydrochloric acid, did not succeed, only the empyreumatic decomposition-products being obtained, which anisoic acid yields when heated by itself.

Anisoate of Soda, $C_{20}H_{17}NaO_{12}$ (dried at 100°).—The salt pre-

pared as above, and purified by repeated crystallisation from hot water, forms perfectly white, indistinct crystals united in nodules. It dissolves readily in water. The analysis gave 8·9 per cent. sodium, agreeing exactly with the formula.

Anisoate of Baryta, $C_{20}H_{17}BaO_{12}$ (dried at 100°).—Prepared by mixing the solution of the soda-salt with the quantity of sulphuric acid exactly sufficient to decompose it; evaporating to dryness over the water-bath; exhausting the residue with absolute alcohol, and digesting the solution (mixed with water) with carbonate of baryta till it was neutralised, the filtered liquid yielded by evaporation easily soluble crystalline nodules resembling the soda-salt.

| | | Calculated. | | Found. |
|------------------------------|-------|-------------|-------|----------------|
| 20 C | . . . | 120 | 39·8 | 39·23 to 39·65 |
| 17 H | . . . | 17 | 5·6 | 5·33 „ 5·54 |
| Ba | . . . | 68 | 22·5 | 22·16 „ 22·75 |
| 12 O | . . . | 96 | 32·1 | |
| <hr/> $C_{20}H_{17}BaO_{12}$ | | 301 | 100·0 | |

Anisoate of Silver, $C_{20}H_{17}AgO_{12}$.—Obtained by decomposing the baryta-salt with sulphate of silver, or by digesting the acid with carbonate of silver. Dissolves readily in water; also crystallises in nodular crystals, and while moist easily acquires a blackish tint.

| | | Calculated. | | Found. |
|------------------------------|-------|-------------|-------|--------|
| 20 C | . . . | 120 | 35·2 | 34·1 |
| 17 H | . . . | 17 | 4·9 | 4·0 |
| Ag | . . . | 108 | 31·6 | 32·2 |
| 12 O | . . . | 96 | 28·3 | |
| <hr/> $C_{20}H_{17}AgO_{12}$ | | 341 | 100·0 | |

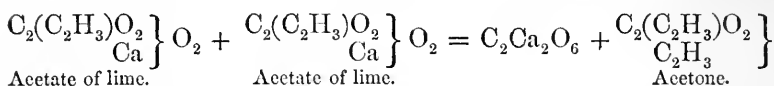
The difference between the experimental and calculated results must be attributed to the tendency to decomposition above noticed.

3. Preparation of Aldehydes from the Acids $C_nH_nO_4$.

It has long been known that when many salts of the acids $C_nH_nO_4$ are heated, they yield, simultaneously with the ketone of the series, a body isomeric with, and in many respects similar to, the aldehyde (propylal, butyral, and valeral); but aldehydes, such as are produced by oxidation of the alcohols, have not yet been obtained from the acids.

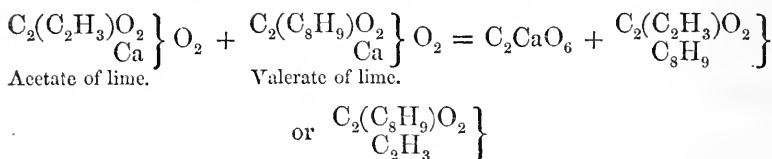
From the existing views of the constitution of the acids $C_nH_nO_4$, and of the ketones and aldehydes, as well as from the decomposition which takes place in the formation of the ketones, we may conclude that the aldehydes must be produced by an analogous process.

The formation of the ketone always requires 2 atoms of the salt.

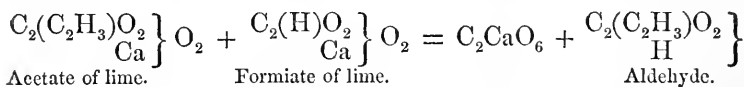


Of 1 equivalent of the acetate of lime there remains only the radical, acetyl [othyl] or formyl-methyl, of the second only the methyl, which unite to form acetone, while the remaining elements form carbonate of lime.

When [as shown by Williamson*] a mixture of the salts of two different acids—*e. g.* valerate and acetate of lime—is heated, the same metamorphosis takes place, 1 eq. of carbonate of lime being formed, and a ketone composed of the radical of the one acid, and the alcohol-radical contained in the other :



If now formiate of lime be heated with the lime-salt of another acid of the series $\text{C}_n\text{H}_n\text{O}_4$, and the mixture subjected to distillation, a ketone is formed, containing an equivalent of hydrogen in place of the alcohol-radical: that is to say, an aldehyde.



In this manner several aldehydes have been prepared by M. Ritter.

Acetaldehyde, $\text{C}_4\text{H}_4\text{O}_2$.—Dry formiate and acetate of lime, mixed in equivalent quantities, were heated in a retort over the open fire; the distillate being received in cooled ether and saturated with ammoniacal gas; crystals of aldehyde-ammonia then separated in considerable quantity. In this operation, especially when considerable quantities of material were used, a quantity of empyreumatic products was also formed, in consequence, partly of imperfect mixture, partly of too high a temperature being applied.

Propylaldehyde, $\text{C}_6\text{H}_6\text{O}_2$.—Propionate of baryta prepared from cyanide of ethyl was mixed with formiate of lime and distilled. Small quantities only were available for the experiment, and the distillate, amounting to only a few grammes, had therefore to be subjected to analysis after two rectifications, in each of which only the first portion was collected. The separation of the aldehyde by

* Chem. Soc. Qu. J. iv. 238.

combination with bisulphite of ammonia could not be effected, because the product was contaminated with propione. The boiling point of the propylic aldehyde used in the analysis lay between 48° and 55° (propylal obtained from butyrate of lime boils at 66°). The analysis gave 58.03 per cent. C, and 10.31 H; the formula $C_6H_6O_2$ requiring 62.0 C, and 10.3 H. The numbers found by analysis would give for the ratio of the equivalents $C : H : O = 6 : 6.2 : 2.5$. As it was impossible to purify the product satisfactorily, the result may be considered as sufficient evidence that propylaldehyde was really formed.

Valeraldehyde, $C_{10}H_{10}O_2$.—Formiate and valerate of lime were distilled together; the portion of the distillate which boiled at about 100° treated with bisulphite of soda; and the resulting sulphite of valeraldehyde and sodium analysed. The analysis gave 31.71 per cent. sulphurous acid, the formula $C_{10}H_9NaS_2O_6 + 3 \text{ eq.}$ requiring 32.13 per cent.

Oenanthol, $C_{14}H_{14}O_4$.—By distilling a mixture of oenanthylate and formiate of lime, an oil was obtained, which combined with bisulphite of soda in crystalline laminae having the appearance of sulphite of oenanthyl and sodium; the oil separated from these crystals by acids possessed the odour of oenanthol.

Caprylaldehyde, $C_{16}H_{16}O_2$.—The distillate obtained from caprylate and formiate of lime exhibited the odour of caprylic aldehyde, and formed a crystalline compound with bisulphite of soda.

Myristate and palmitate of lime distilled with formiate of lime yielded very offensive products, which were for the most part oily, and deposited only small quantities of solid substances. The latter, after pressure and repeated crystallisation from hot alcohol, consisted of small, perfectly white, inodorous crystalline scales, but yielded by combustion much larger quantities of carbon and hydrogen than is consistent with the composition of myristic and palmitic aldehyde. Probably these aldehydes cannot exist at the high temperature required to decompose the mixed salts.

The preparation of the aldehydes by this method will not, perhaps, be often advantageous; because empyreumatic products are formed at the same time in rather considerable quantity; and the presence of these products prevented the oenanthylic and caprylic aldehydes from being purified sufficiently for analysis; or the experiment should have been made on a much larger scale. Perhaps the occurrence of these impurities may be prevented by heating the saline mixture in an oil-bath, the temperature being maintained as little as possible above that which is required for the decomposition.

On Anisic Alcohol.*

By S. Cannizzaro and C. Bertagnini.

Cannizzaro† found that hydride of benzoyl, $C_{14}H_6O_2$, when treated with an alcoholic solution of potash, is converted into benzoic acid and the corresponding alcohol $C_{14}H_8O_2$. According to Cannizzaro and Bertagnini, hydride of anisyl, $C_{16}H_8O_4$, is in like manner converted into anisic acid, $C_{16}H_8O_6$, and a corresponding alcohol, $C_{16}H_{10}O_4$, viz. *anisic alcohol*.

To prepare the hydride of anisyl, anisol is gently boiled for an hour with about three times its volume of dilute nitric acid of 14° Baumé, after which the heavy oily product is washed with water, then with dilute potash-ley, and distilled. To separate the hydride of anisyl from the accompanying substances, the distillate is shaken up with a warm solution of bisulphite of soda of 30° Baumé; the resulting crystalline compound left to drain after cooling; washed with alcohol till it is perfectly white, and the alcohol which runs off no longer becomes turbid when mixed with water; the compound then dissolved in the smallest possible quantity of hot water, and heated with an excess of strong solution of carbonate of potash. The hydride of anisyl, which separates in the form of an oily layer rising to the surface, is then taken off and freed from any saline liquid that may be enclosed in it, by distillation.

When hydride of anisyl thus prepared is dissolved in an equal volume of alcohol, and this liquid mixed with three times its bulk of alcoholic potash-solution of about 7° Baumé, an action takes place attended with slight evolution of heat; and anisate of potash separates out in such quantity that the liquid solidifies to a crystalline pulp. After 10 or 12 hours, the alcohol is distilled off in the water-bath, the residue diffused in water, and the liquid heated with ether to extract the anisic alcohol, which, after the evaporation of the ether, remains in the form of a brown oil. On distilling this oil, a colourless liquid passes over at about 260° C, which, if the temperature of the air is low, soon crystallises: this product is anisalic alcohol. When thus prepared it generally retains a portion of unaltered hydride of anisyl, which may be easily recognised by its power of forming crystalline compounds with concentrated solutions of alkaline bisulphites. To remove this impurity, the preparation must be again treated with a small quantity of alcoholic potash-solution, then distilled in a stream of

* Il nuovo Cemento, i. 99; Ann. Pharm. xcvi. 188.

† Chem. Soc. Qu. J. vii. 192.

carbonic acid, and the distillate, after solidifying, pressed between filtering-paper.

Pure anisic alcohol thus prepared distils without decomposition at 248° to 250° C; melts at about 23° when anhydrous, but at a lower temperature (as low as 7°) when moist. Crystallises in hard shining needles.

| Calculated. | | | Found. | | | |
|-------------------|-----|--------|--------|--------|--------|--------|
| 16 C | 96 | 69.56 | 69.21 | 69.51 | 69.32 | 69.60 |
| 10 H | 10 | 7.24 | 7.33 | 7.30 | 7.37 | 7.30 |
| 4 O | 32 | 23.20 | 23.46 | 23.19 | 23.31 | 23.10 |
| $C_{16}H_{10}O_4$ | 138 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

Anisic alcohol is heavier than water; has a faint spirituous and sweetish odour, and a burning taste resembling that of oil of aniseed. It does not alter by exposure to the air at ordinary temperatures, even for a long time; but when heated nearly to its boiling point, it absorbs oxygen, and is converted into hydride of anisyl.

Oxidising substances convert anisic alcohol, with the greatest ease, first into hydride of anisyl, then into anisic acid. In contact with platinum-black, it emits, after some time, the odour of hydride of anisyl, and after a few days the entire quantity of the anisic alcohol is converted into anisic acid. Dilute nitric acid, with the aid of heat, likewise brings about these changes in succession.

Anisalic alcohol heated with various salts, *e. g.* benzoate, anisate, and acetate of potash, dissolves them, but deposits them again on cooling. It likewise dissolves several organic substances, *e. g.* salicic, phillyrin, and hippuric acid.

Potassium introduced into liquid anisic alcohol causes an evolution of hydrogen, which becomes very violent on the application of heat. The resulting potassium-compound remains dissolved in the yellow liquid while warm, but the whole solidifies into a buttery mass on cooling.

Sulphuric acid, even when but moderately concentrated, converts anisic alcohol into a reddish resinous mass. Anhydrous phosphoric acid exerts a similar action. When the alcohol is moderately heated with chloride of zinc, a violent action takes place; water is formed, which unites with the chloride of zinc, and an oily liquid rises to the surface, which on cooling solidifies in a hard transparent, vitreous mass, melting at 100° , insoluble in water and alcohol, but soluble in sulphide of carbon.

Chlorine gas passed into anisic alcohol is absorbed, with evolution of heat, the liquid becoming turbid, and ultimately sepa-

rating into two layers, the lower of which is aqueous hydrochloric acid, while the upper appears to be the chlorine-compound of the radical contained in the alcohol. This upper liquid, when quickly washed with a dilute solution of carbonate of potash, and then with water, forms a colourless oil, having a fruity odour and burning taste. In contact with an alcoholic solution of ammonia, it is quickly decomposed, with formation of sal-ammoniac and a liquid which exhibits all the properties of anisic alcohol. This substance appears also to undergo a similar decomposition in contact with solutions of alkaline carbonates. It was not obtained in sufficient quantity for analysis. Want of material likewise prevented the formation of other compound ethers from anisic alcohol. In an attempt to prepare anisic ether by the action of chloride of anisyl on the alcohol, a violent action was observed, attended with abundant evolution of hydrochloric acid vapours, and formation of anisic acid, and a resinous substance insoluble in alcohol and ether, but soluble in chloroform.

Hydride of salicyl (salicylous acid), $C_{14}H_6O_4$, treated with potash in aqueous or alcoholic solution, either at high or at low temperatures, combines with the alkali, without undergoing further alteration when heated; it is only when the potash-hydrate has become solid by evaporation, and then melts at the higher temperature, that the salicylate of potash formed at the beginning of the action is converted, as is well known, into salicylate. This process, therefore, does not yield the alcohol corresponding to salicylic acid. The composition proper to this alcohol is exhibited by saligenin, which likewise behaves like an alcohol in certain points (conversion into an aldehyde, the hydride of salicyl by certain oxidising agents; and conversion into salicylate of potash, with evolution of hydrogen, when heated with hydrate of potash), but neither possesses the volatility of other alcohols, nor forms ethereal compounds with acids.

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XI.—*On Cadmium-ethyl.*

By J. A. WANKLYN,

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THE close analogy subsisting between zinc and cadmium led me to expect that the latter would form a compound with ethyl corresponding to zinc-ethyl. In consequence of this expectation I instituted a preliminary experiment, which satisfied me that such is really the case. I then referred to the journals,* and saw that already, in 1853, Schüller had made an investigation with a similar object in view, but that he had altogether failed in the attempt. In the account which he has published of his experiment one or two little omissions struck me, which omissions, I believe, caused him to arrive at no positive result.

These considerations at once determined me to pursue the subject, and accordingly I made a number of preliminary experiments on the action of cadmium on iodide of ethyl mixed with ether. Several times in the course of these experiments I obtained undoubted proof of the existence of a body containing cadmium in combination with organic matter, and volatile below 200° C. In order to procure a sufficient quantity of the new substance for an examination of its properties, I resolved on performing an experiment on a large scale, which experiment I now describe at length.

* Ann. Ch. Pharm., lxxxvii., 56, 57.

About 2,000 grains of cadmium was beaten out into a thin lamina, which was then cut up by means of scissors into very narrow strips. Thus prepared, the metal was introduced into the copper digester used in the manufacture of zinc-ethyl. Perfectly dried iodide of ethyl and ether, 1,000 grains of the former and about an equal bulk of the latter, were next poured in. Then the digester was closed air-tight, and heated up to 130°C . for about an hour. The temperature was next lowered to 100°C . and not suffered to rise above that point during the remainder of the digestion. The whole time occupied by the digestion was about 50 hours, but this process was not continued uninterruptedly throughout that period, as the operation was arrested at night. Having completed this part of the process, the digester was allowed to cool, and afterwards opened by removing the screw-plug. Immediately a considerable quantity of gas escaped. A bent tube was then adapted, and the distillation made in an atmosphere of dry carbonic acid, just as recommended by Frankland in his memoir on zinc-ethyl. The disposition of the apparatus, and the general mode of performing this experiment, were such as Frankland has detailed in his memoir on zinc-ethyl, and to that paper I refer.*

During this distillation, a large quantity of ether and iodide of ethyl came over, but no fumes were evolved at temperatures below 170°C . When the temperature had reached 160°C . the receiver was changed, and between 180°C . and 220°C . a colourless fuming liquid distilled. This liquid, when exposed to the air, evolved first white fumes, and then brown fumes, owing to the formation of oxide of cadmium, and finally burst into flame, depositing brown spots on neighbouring objects. It effervesced with water, forming at the same time a white precipitate. In this respect it resembles zinc-ethyl, as also by the formation of a white solid on the slow absorption of oxygen. Its smell was peculiar, and not disagreeable, rather like that of zinc-ethyl. An estimation of cadmium was made by treatment with water. The precipitate so obtained was dissolved in dilute nitric acid, and the resulting solution evaporated to dryness, and finally ignited, when it left a residue of the deep brown colour characteristic of oxide of cadmium.

Treated in this way, 0.2085 grammes of the liquid gave 0.0877 grammes of oxide of cadmium. As a test of the purity

* Transactions of the Royal Society, 1855, p. 259.

of the oxide of cadmium, it was converted into chloride of cadmium, and weighed in that form, with these results :

| Calculated. | Found. |
|-------------|-------------|
| 0·0877 CdO | 0·0877 CdO |
| 0·1250 CdCl | 0·1255 CdCl |

The foregoing analysis proves that the distillate contained 36·78 per cent. of cadmium, which indicates that the substance was impure. This circumstance was by no means unexpected, as the total amount of distillate which came over above 160° C. did not much exceed one gramme and a half, and so small a quantity would be rendered very impure by the residual vapour of ether in the digester. If we take the formula of the new substance to be $\text{Cd C}_4 \text{H}_5$, the distillate would contain 55·92 per cent. of this substance. The remainder of the percentage would be ether, iodide of ethyl, and perhaps hydrocarbons—the result of the decomposition of this cadmium-ethyl whilst it was in the digester.

In order to obtain the new substance pure, the obvious course was to redistil the crude product, and endeavour to obtain a constant boiling point. For that purpose, more crude cadmium-ethyl was requisite. As the action in the digester had been very far from complete, the ether and iodide of ethyl which had come over first were poured back, along with a further quantity of these ingredients, into the digester, which was closed and heated to 125° C. for two or three days.

On submitting the product to distillation, the ether which came over below 170° C. was collected apart, and the receiver changed after the white fumes had been observed for some time. This second part of the distillate, which fumed as in the former operation, was redistilled in the oil-bath, but no constant boiling point could be obtained. The liquid boiled or evolved gas rapidly up to 165° C., indicated by a thermometer placed in the vapour, and deposited metallic cadmium on the sides of the flask, although the temperature of the surrounding oil-bath was never higher than 210° C. What came over between 95° C. and 165° C. was collected apart, and was found to be greatly altered in properties and composition. On exposure to the air, it fumed a little, but would not inflame spontaneously. Subjected to analysis it gave the following results: 0·093 grms. on treatment with nitric acid and subsequent ignition, yielded 0·0118 grms. of residue. In a second experiment 0·3228 grms. of substance gave, when similarly treated, 0·0387 grms. of residue. These residues, unlike that pre-

viously mentioned, contained, in addition to the oxide of cadmium, a quantity of oxide of zinc, and, instead of being brown, were white.* A combustion with oxide of copper was also made, wherein 0·1852 grms. of substance gave 0·4218 grms. of carbonic acid, and 0·1962 grms. of water.

Here are the collected per centage results of these analyses:

| | I. | II. | III. |
|-------------|-------|-------|-------|
| CdO and ZnO | 12·69 | 11·99 | |
| C | | | 62·11 |
| H | | | 11·77 |

These numbers show that distillation decomposes in great part the ethyl-compound of cadmium.

The changes which ensue during the action of the materials in the digester present some points of interest, and were made the subject of study. Perfectly dry cadmium, ether, and iodide of ethyl, were sealed up in a glass tube, which was then placed in the water-bath, and frequently agitated during the digestion. For the first five hours there was no visible action. During the next ten hours some crystalline powder was deposited, afterwards the action seemed very rapid; the cadmium underwent great diminution in volume, and a large quantity of shining powder occupied the tube. This powder appeared more soluble in the liquid within the tube whilst hot than when cold. On breaking the tube and bringing out the contents into the air, they did not fume at all; very unlike the behaviour of the resulting oily body which exists in the digester previously to the distillation of zinc-ethyl. Yet this powdery substance, which did not fume, became hot on exposure to the air, and effervesced violently with water, giving a precipitate soluble in acids. In the distillation of cadmium-ethyl, as I have many times noticed, no fumes are given off until a temperature of about 170° C. has been attained; whilst with zinc-ethyl, hardly any of the ether distils before the fuming on exposure to air commences. These facts go to prove that, as first formed, and previously to distillation at 170° C., the cadmium-ethyl exists in stable combination with iodide of cadmium. In the case of zinc, there is a feeble compound of iodide of zinc with zinc-ethyl, as was pointed out by Frankland.† But a tempera-

* The appearance of zinc in this situation rather surprised me, as the cadmium employed in the experiments was almost absolutely free from zinc. Furthermore, I made an experiment some time ago on the behaviour of brass filings on iodide of ethyl at 150° C. I found that there was no action.

† Transactions of the Royal Society, 1855, p. 263.

ture which almost utterly breaks up the zinc compound into zinc-ethyl and iodide of zinc, fails to resolve the corresponding cadmium body into its proximate constituents. Some attempts were made to obtain this double compound of cadmium-ethyl with iodide of cadmium in a state of purity, but without success, as no means of separating the free iodide of cadmium from the double compound presented themselves. Ether dissolves iodide of cadmium slightly, especially under pressure, and ether appears to behave similarly with the double compound.

The contents of the digester, after the cadmium-ethyl had been distilled off in the experiment on the large scale, were examined. They consisted of cadmium unchanged and a grey powder. This residue was treated with hot water, and filtered. The filtrate was evaporated to dryness, and the solid product powdered and dried at a temperature considerably above 100°C . It proved to be pure iodide of cadmium, and gave the following results on analysis:

| | | Calculated. | | Found. |
|----|-----|-------------|--------|--------|
| I | . . | 126.88 | 69.48 | 69.42 |
| Cd | . . | 55.74 | 30.52 | 30.29 |
| | | <hr/> | <hr/> | <hr/> |
| | | 182.62 | 100.00 | 99.71 |

The residue on the filter from which the iodide of cadmium had been washed out contained some oxyiodide of cadmium, which, in all probability, was an after product, due to the reaction of finely-divided metallic cadmium on iodide of cadmium when exposed to air and moisture. This insoluble grey powder, which has obviously its origin in the decomposition of cadmium-ethyl previously formed, was very considerable in quantity; a fact which proves that a considerable amount of cadmium-ethyl had been in existence at some period of the operation.

In the experiments on the large scale, about 100 grammes of iodide of ethyl had been employed in the two operations, yet the entire amount of cadmium-ethyl which distilled over in these operations could not exceed 3 grammes. It follows, therefore, that a large proportion of cadmium-ethyl had been decomposed.

Seeing that the contents of a tube—in which cadmium has been digested with iodide of ethyl and ether in the water bath—are a white shining powder previously to distillation, and seeing that products examined subsequently to distillation consist of a

grey powder, I am entitled to conclude that this decomposition of the cadmium-ethyl goes on to a great extent during distillation.

I have arrived at the conclusion that the temperature required to decompose the double compound of iodide of cadmium and cadmium-ethyl breaks up nearly all of the cadmium-ethyl, a small proportion only of that substance being carried over unchanged by the hydrocarbons generated in that decomposition.

As cadmium-ethyl will not distil at ordinary pressures without undergoing decomposition, it was suggested to me by Professor Frankland that cadmium-methyl would be a more favourable body for investigation than the subject of this memoir; and as the presence of iodide of cadmium is a troublesome complication, it was likewise suggested that an alloy of sodium and cadmium should replace cadmium in the proposed experiments.

It has occurred to me also that the employment of an alloy of cadmium and zinc cannot fail to yield interesting results, which may throw great light upon the mode of formation and composition of this class of bodies. This last-mentioned train of research is already in progress, and that named immediately before will be begun as soon as practicable.

No one who reads this paper will doubt that the discovery of zinc-ethyl was an indispensable preliminary to that of cadmium-ethyl. To Professor Frankland for that, and assistance of a more personal nature, I return thanks.

XII.—*On a Coal-Gas Carbon and Nitric Acid Voltaic Battery.*

BY JAMES L., AND L. WHEELER.

It will be readily acknowledged that Grove's nitric acid and platinum battery is hitherto unequalled for the quantity and tension of the electricity evolved. It may, therefore, be regarded as the instrument of standard excellence. The great expense of the platinum, is, however, an obstacle to its general introduction. Many years ago, the late Mr. JOHN THOMAS COOPER first suggested the use of carbon in the construction of the voltaic apparatus, and Professor Bunsen is known to have followed in the same

track. Bunsen's battery is made with a great amount of trouble; and, when constructed, is liable to objections, particularly that, after some use, it becomes inefficient from the porosity of the carbon, which causes the rapid corrosion of the metallic connexions.

Ordinary graphite is a form of carbon, remarkable for its high power of conducting electricity, and we made many experiments for applying it as the receiving surface in the nitric acid battery. The difficulties of this application soon showed themselves to be insuperable. In the first place, small plates only of this substance are obtainable, many of which were entirely disintegrated as soon as they were brought into contact with nitric acid: its brittleness also is such as to render it unmanageable. Having abandoned the common graphite battery, our attention was next turned to a modification of Daniell's, by bringing the zinc and copper plates much closer together than in his original form of apparatus. The quantity of sulphate of copper, dissolved by dilute sulphuric acid, is soon decomposed by the hydrogen eliminated from the zinc plate, hence the necessity of a constant supply of the salt to keep up the saturation of the acid. In one experiment with two pairs of Daniell's cells, excited by dilute sulphuric acid, saturated with sulphate of copper, there was only a slight spark between points of carbon, and hardly any perceptible decomposition of water. The copper plates used in this instance measured $5\frac{1}{2}$ inches by 3, and were surrounded in an outer cell by a double zinc plate, well amalgamated. No amount of platinum wire could be ignited by this arrangement. To maintain a large supply of oxide of copper in solution, recourse was had to the nitrate, a salt so much more soluble than the sulphate. In this instance, a very manifest increase of power was obtained, as an inch of fine iron wire was ignited by two pairs of cells, while with the sulphate no such effect was produced. A saturated aqueous solution of the nitrate was employed.

Our attention was next directed to the application of the carbon deposited in the interior of coal-gas retorts, as the receiving surface in a cell with nitric acid, this carbon being liable to no disintegration from contact with acids.

Difficulties were at first apprehended in procuring plates of sufficient size. We found, however, that it could be readily sawn across in the thinnest direction, by the aid of a piece of cast iron and sharp sand; the plate could then be finished by grinding it with sand upon a stone. As entire plates of the coal-gas carbon

could thus be obtained, we introduced two of them into cells with nitric acid. The shape of these plates was slightly irregular, their dimensions being nearly $5\frac{1}{2}$ inches by 3. Five inches of platinum wire, of the 50th of an inch diameter, were heated to dull redness, and, from the mean of three experiments, 1.9 cubic inch of the gases, from the decomposition of water, were collected in 4 minutes 43 seconds, a strong solution of carbonate of potash being employed with iron electrodes.

These two pairs of plates were compared with two pairs of Grove's, with platinum plates of the same dimensions as those of the carbon. The two pairs of Grove's plates evolved from the same solution 1.9 cubic inch of gases in 4 minutes 45 seconds, or 2 seconds more than with the carbon plates. The same length of the same platinum wire was ignited in each case. In these two experiments the greatest care was employed in inserting as many pieces as possible of amalgamated zinc plate between the generating plate and porous cell, by which means the internal resistance to the current was reduced to a minimum. The plates of gas carbon were connected by slips of platinum foil, supported above by slips of sheet zinc, which served to give them strength, and increase their conducting power by keeping them cool. The dilute sulphuric consisted of five measures of water and one of acid. The nitric acid was the ordinary material of commerce.

On one occasion, the immersion of the plates in the acids was continued for six hours without any material diminution of power.

XIII.—*Description of a Self-acting Washing Bottle.*

BY WILLIAM STEPHENS CLARK,

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In the "Philosophical Magazine" for August, 1849, a simple apparatus for washing precipitates is described by Mr. Summers, which acts by an adaptation of two concentric tubes to the lower extremity of a washing bottle.

The following apparatus is founded on the same principle; but

the concentric tubes, being passed through a cork at the top of the reservoir, the instrument is perhaps more convenient for general use.

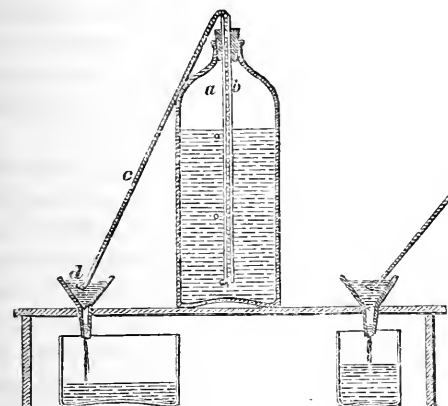


Fig. 1.

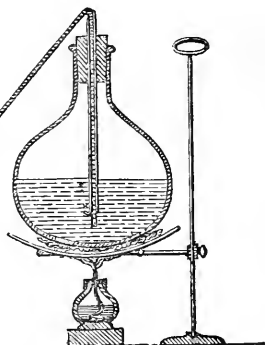


Fig. 2.

A wide tube (*b*) is inserted in the cork of a bottle (*a*), so as nearly to touch the bottom. A narrow tube (*c*) is bent into the form of a syphon, the shortest limb of which is a little longer than the wide tube, and the other of such a length that when the short one is perpendicular, the two ends of the tube will be on the same level. The end of the longer limb (*d*) is slightly recurved, in order that the water may not disturb the precipitate.

The bottle is now filled with water, the cork fitted tightly in, and it is placed so that the bottom of the wide tube may be below the edge of the filter paper in the funnel. The narrow tube is placed inside the wide one as in the drawing; then by blowing down the wide tube, water is forced up through the syphon into the funnel, but will not be able to rise above the level of the bottom of the wide tube, and consequently cannot reach the top of the filter paper.

If, instead of a bottle, a thin glass receiver is used (Fig. II.), heat may be applied, and the water in the funnel will be kept warm; but care must be taken not to allow the water to boil, as in that case the water would be forced too fast through the syphon, and might overflow the wide tube, and crack the receiver.

XIV.—*On the Composition of some Varieties of Foreign Iron.*

By F. A. ABEL,

DIRECTOR OF THE CHEMICAL ESTABLISHMENT OF THE WAR DEPARTMENT.

THERE are few subjects of practical importance that have, during the last twelve months, attracted general attention in this country to the same extent as the question of the manufacture of iron ordnance. While numerous plans have been proposed, discussed, and tried for constructing cannon, either of wrought-iron, steel, or mechanical combinations of iron-material of different kinds, which shall be capable of throwing larger and heavier projectiles than those hitherto used, the question at issue has gradually become one of more general interest, involving considerations intimately connected with the metallurgy of iron, in consequence of the conclusions deduced from the experience in the late war, that the conditions necessary for obtaining a durable and uniform material for iron guns are as yet far from being fully determined.

The American Government has lately published a collection of reports, containing some interesting and important observations connected with the manufacture of iron ordnance, though it does not appear that the researches carried on in that country, or the experience gained by the directors of gun foundries belonging to various continental states, have as yet effected much more than the provision of a number of data relating to the nature and quality of iron employed, the different methods of treating the metal and of casting the gun, and the effects of mechanical tests and of the explosive force of powder upon iron ordnance. There is little doubt that the accumulation of such data, and extensive experiments suggested by their comparison, will ultimately lead to the establishment of the conditions necessary for insuring to iron ordnance uniformity and durability.

The collection in this country of such data as those referred to has hitherto been a matter of great difficulty, from the circumstances that iron ordnance were obtained by Government from various private sources; that no special conditions have been observed in the selection or treatment of metal for ordnance; that no records of the material employed by the different manufacturers have been preserved, and that no system of tests, physical or chemical, has been applied to the metal composing the guns, beyond the regulation proof to which ordnance were submitted before their acceptance from manufacturers. It is obvious also, from these

circumstances, that no uniformity in the iron guns used in this country could be expected.

Now that Government has determined to take the manufacture of iron ordnance into its own hands, the most serious obstacles to the perfection of these important arms in England are set aside, and the introduction of a complete system of testing and of record, together with the results of a very extensive series of experiments, on a sufficient scale, which have already been commenced, will, it is hoped, furnish important contributions to our knowledge of the constitution and mode of treatment of iron, best adapted for the manufacture of ordnance.

In carrying out the system of experiment determined upon by Government, attention has been directed, in the first place, to iron reduced from its ores by charcoal, this being the material employed exclusively, in some continental States, and to a very great extent in others, in the manufacture of iron ordnance. Much stress is laid, by many authorities on the continent, upon the greater fitness, for this purpose, of that description of iron than of the best hot-blast, or even of cold-blast iron, smelted with coal or coke. It appeared, therefore, naturally the first step, in comparative experiments with various materials, to ascertain the nature of the iron composing the most durable guns manufactured in those countries, and to determine, by comparative experiments here, whether guns manufactured from charcoal-iron exhibit great superiority over those made *according to the same system* of iron reduced from its ores by mineral fuel. Various specimens of foreign charcoal-pig-iron, and cannon of that metal made in France, Belgium, and Sweden, have been collected for comparative examination, and considerable quantities of charcoal-iron, procured from Nova Scotia, Sweden, and America, have been purchased, for experimental purposes. The results obtained, up to the present time, are principally those furnished by the analysis of several of these specimens; and I venture to submit these to the Chemical Society, as they exhibit some points of interest, and may also serve, to others engaged in similar inquiries, as additional means, to those already existing, of comparing the constitution of the varieties of charcoal-iron with that of other descriptions of iron.

It is unnecessary, in the present instance, to enter into analytical details; but, as various methods are employed, by different chemists, for determining the most important constituents in iron, it may be advisable to furnish a brief outline of those adopted in performing the subjoined analyses.

The *graphite* was determined by digesting the finely-pulverized iron with concentrated hydrochloric acid, and boiling the residue for some time with a moderately-strong solution of potassa: the graphite was collected, washed, dried, and weighed. It was afterwards placed in a capsule and heated to redness in a muffle, until the whole of the carbon was burnt off. The weight of the slight incombustible residue which was generally obtained was deducted from the weight of the graphite.

For the determination of the *total amount of carbon* the iron was reduced to an extremely fine state of division; it was then first mixed with about twice its bulk of fine sand, or powdered glass, and afterwards with a mixture of chromate of lead and chlorate of potassa. The combustion was conducted in the usual manner, a current of oxygen being frequently employed.

The proportion of *silicium* was ascertained by acting upon the finely-divided metal with concentrated hydrochloric acid, evaporating to dryness, and digesting the residue with hydrochloric acid. The insoluble portion was collected upon a filter, washed until free from iron, dried, and ignited until the whole of the carbon was burnt off. The silicic acid thus obtained was digested with solution of potassa, after its weight had been determined. If any insoluble residue was obtained its weight was deducted from that of the silicic acid.

To determine the proportion of *sulphur*, hydrochloric acid was allowed to act very slowly upon fragments of the iron, in a suitable apparatus, and the gas generated was passed through a slightly acid solution of acetate of lead. The sulphide of lead produced was collected, washed, and ultimately weighed as sulphate of lead.

The *phosphorus* was determined by digesting, in nitrohydrochloric acid, fragments of the metal, of the size of small peas, evaporating the solution to dryness, digesting the residue with hydrochloric acid, and separating the insoluble from the soluble portion. The hydrochloric solution was partly neutralised by sesquicarbonate of ammonia, and the greater part, if not the whole, of the sesquichloride of iron reduced to protochloride, by sulphite of ammonia. Solution of acetate of ammonia was then added in excess, and afterwards a small quantity of solution of sesquichloride of iron. The phosphate of iron was precipitated by boiling, collected, and dissolved in hydrochloric acid, and decomposed by sulphide of ammonium. The phosphoric acid was estimated in the usual manner, as pyrophosphate of magnesia.

In the following table is represented the percentage composition

of several specimens of iron, reduced from its ores by charcoal, as calculated from the analytical results:—

TABLE I.

Composition of Pig Iron smelted with Charcoal obtained from

| | NOVA SCOTIA. | | | AMERICA. | | | FRANCE. | SILESIA. | |
|--------------------------------|--------------|----------|--------|----------|----------|--------|---|--|--|
| | Grey. | Mottled. | White. | Grey. | Mottled. | White. | Grey. | White, <i>very crys- talline.</i> | White, <i>less crys- talline.</i> |
| Specific gravity... | 7.120 | 7.540 | 7.690 | 7.159 | 7.540 | 7.675 | 7.000 | 7.531 | 7.604 |
| Iron..... | 95.20 | 95.35 | 95.25 | 94.87 | 96.35 | 96.55 | 95.18 | 93.45 | 90.75 |
| Combined Carbon | — | 1.72 | 2.96 | .04 | 1.14 | 2.79 | — | 4.94 | 3.62 |
| Graphite..... | 3.11 | 1.38 | — | 3.07 | 1.50 | — | 3.40 | — | — |
| Silicium | 1.11 | .26 | .21 | 1.80 | .79 | .32 | .80 | .75 | .25 |
| Sulphur | .01 | .03 | .02 | trace | .01 | .06 | .03 | trace | trace |
| Phosphorus | .13 | 1.30 | 1.53 | .22 | .20 | .17 | .45 | .12 | 3.26 |
| Manganese | .25 | trace | — | trace | trace | trace | — | 5.38 | 2.00 |
| Copper | — | — | — | trace | trace | trace | — | .24 | trace |
| Traces of Titanium and Cobalt. | | | | | | | Traces of Arsenic and Chromium | Traces of Cobalt. | |

The specimens of white iron from Silesia differ from one another in several respects, and to such an extent, as to prove that they were obtained from different ores. Both were very hard and brittle; but the ore containing the largest amount of manganese exhibited a foliated structure and brilliancy of lustre, very similar to that of refined antimony, while the other specimen, rich in phosphorus, was less brilliant and far more compact. These irons were proposed for admixture with dark grey iron; but it was considered that they could not be advantageously employed for this purpose.

The French iron examined was a specimen of the metal reduced by charcoal from hæmatite-ores, at the Government cannon foundry of Ruelle, and employed exclusively in admixture with charcoal-iron also reduced from similar ores in the neighbourhood, for the manufacture of ordnance. It was dark, soft, fine-grained, and uniform in texture. In its general characters it was similar to

the Swedish grey iron analysed, though exhibiting a superiority over the latter in reference to the amount of silicium it contains.

The specimens of American and Nova Scotia iron analyzed were taken as average samples from large parcels of the metal purchased by Government for experimental purposes.

The different varieties of iron from each source exhibit such differences in their composition as are generally observed in irons reduced from the same ore under modified conditions. Both the Nova Scotia and American irons are of excellent quality, and furnish the best results when submitted to physical tests. Comparative trials are about to be made of their merits as gun-metal.

The subjoined table exhibits the results of the analyses of four specimens, from guns of foreign manufacture.

TABLE II.

Composition of Iron Gun Metal from

| | BELGIUM. | FRANCE. | SWEDEN. | RUSSIA. |
|------------------------|---|-----------------------------------|------------------------|-------------------|
| Specific gravity | 7·250 | 7·250 | 7·050 | 7·135 |
| Iron | 95·61 | 96·02 | 95·87 | 94·36 |
| Combined Carbon | ·78 | 1·03 | ·18 | ·47 |
| Graphite | 2·12 | 1·87 | 2·62 | 2·83 |
| Silicium | ·99 | ·35 | 1·19 | 1·10 |
| Sulphur | ·06 | ·03 | ·08 | ·02 |
| Phosphorus | ·29 | ·45 | ·11 | ·37 |
| Manganese | ·15 | ·25 | trace | ·85 |
| Titanium | traces | traces | trace | trace |
| | Traces of Chromium, Arsenic, Zinc, and Copper. | Traces of Chromium and Tin. | Traces of Chromium. | Traces of Tin. |

The Swedish metal examined has great resemblance to that composing the Russian gun which was one of those lately captured and selected for experiment. A severe proof to which this gun was submitted showed that the metal composing it was of excellent quality.

The Swedish metal was of a uniform light grey colour, while the Russian gun exhibited a slightly mottled appearance. Both contained the graphite in a finely divided state. It is worthy of remark, that the strength and durability of Swedish iron guns is found to be variable; which circumstance is ascribed to the very

general practice of casting the guns directly from the blast furnace, instead of first submitting the metal to treatment in reverberatory furnaces.

The specimen of French gun-metal was obtained from the cannon foundry at Ruelle. It resembled, in a remarkable manner, several specimens of iron gun-metal obtained from the cannon foundry at Liège, of which the composition of an average sample is also given in the above table. Both kinds were mottled iron of very uniform character, exhibiting a short and regular fracture, and a fine and compact structure. Their specific gravities are identical, and the differences exhibited in their composition are but slight. For the preparation of the French gun-metal, a mixture of various descriptions of charcoal pig-iron, obtained at Ruelle, is made with grey pig-iron, from other similar iron works in the neighbourhood (*e.g.* from *La Chapelle* and *Etouars*) with old French cannon, and with the "dead-heads" from former castings. By a protracted treatment in reverberatory furnaces, these metals undergo thorough mixture, and purification at the same time, and are converted into the uniform mottled metal above referred to. The fuel used for the remelting and mixing is Newcastle coal.

At the Belgian Government cannon foundry a certain proportion of hot-blast iron, smelted with coke, is employed in admixture with old cannon, "dead heads," and charcoal pig-iron, obtained from various smelting works, more particularly in the neighbourhood of Charleroi. The fuel used for the remelting is a semi-anthracite coal, from Belle Vue, in the neighbourhood of Liège, and has the following percentage composition:—

| | | | | | |
|----------|---|---|---|---|-------|
| Carbon | . | . | . | . | 85.56 |
| Hydrogen | . | . | . | . | 4.20 |
| Oxygen | . | . | . | . | 2.40 |
| Nitrogen | . | . | . | . | 1.92 |
| Sulphur | . | . | . | . | 1.00 |
| Ash | . | . | . | . | 4.92 |

The percentage of phosphoric acid in the ash is 1.60.

The same care is taken to ensure the production of a metal of uniform structure, as at Ruelle; and the excellent results obtained by the proof of the guns, and by the mechanical tests to which the metal is submitted, bear very strong evidence in favour of the superiority of iron of the particular constitution and structure produced in Belgium and France, for the manufacture of guns, over other kinds of iron, even equal to it in chemical quality.

Unquestionably the repeated exposure of grey iron to a moderately oxidising action, in the reverberatory furnace, has the effect of improving its quality, and of removing one of the impurities most objectionable in iron which is to possess tenacity and elasticity, namely, silicium. In experiments lately made, in connection with some patent processes for improving the quality of iron, it was found that the oxidising action of air upon highly-heated iron had the effect of removing the silicium entirely, before the amount of carbon existing in the metal was diminished in any sensible degree. The close-grained and very uniform structure of the iron produced by the mixing and remelting processes, on the continent, and the very finely divided condition in which the graphite exists in the iron, are elements affecting the durability of the gun-metal, of equal importance to the purity of iron. Some pieces of iron ordnance which have either burst upon proof, or after having been but a short time in use, and the metal composing which was of good quality and even of an unusually pure description, evidently owed their incapability to resist the force of gunpowder to the comparatively loose structure of the metal, and to the existence of the graphite in large scales. There are, moreover, various points to be taken into consideration, in connection with the *method of casting guns*, which cannot be entered into here; but which, doubtless, greatly influence their physical structure and, consequently, their durability.

It would be premature to attempt a comparison between the merits of charcoal-iron and those of the better qualities of British cold-blast iron, as materials for ordnance, from results of analysis alone; but thus much is certain, that iron smelted with mineral fuel may be obtained in abundance in this country, which contains not more phosphorus or sulphur than are found in average specimens of charcoal-iron, and that abundant proofs already exist of the ease with which silicium may be removed from pig-iron, by judicious treatment. It may, therefore, be confidently expected that future experiments on the casting of ordnance, with various kinds of iron, will prove that we are not dependent upon a supply of charcoal-iron, for the production of durable guns.

As an appendix to this communication, I beg to lay before the Society the results of analysis of a specimen of the cast steel manufactured by Krupp, of Essen, of which such beautiful specimens were exhibited at the Paris Exposition of 1855.

This cast-steel was proposed, by M. Krupp, as a material for ordnance, as far back as 1847, and the first small gun (a 3 pr.)

cast of it was submitted to very severe tests, in Berlin, in 1849, and finally proved to bursting. A 12-pr. gun, of the same material, was afterwards sent for trial to this country (early in 1855), after having likewise withstood very severe tests. At about the same time, a cylinder of the cast steel was sent from Essen, and bored by Messrs. Walker, of the Gospel Oak Works, to the calibre of an 8-inch gun. Its breech was fitted with a cast-iron case, or jacket, the thickness of which was 10 inches at the breech, and 8·5 in front of the trunnions. The weight of the gun complete was 8 tons 5 cwt. The case was in contact with the steel barrel only at its two extremities, at the breech and the middle of the barrel; at the latter place a wrought-iron wedge-ring was fitted into the barrel, and fixed to the jacket by screws. This gun was proved at Woolwich, but burst the first time it was fired. The probable cause of this unexpected result has been a subject of some public discussion in Germany, but there is little doubt that it was due to the injudicious form of projectile (weighing 259 lbs.) which the parties who proposed to Government the experiments with cast steel, and provided the gun for trial, insisted upon employing for the proof.

The gun was broken into ten large pieces and a number of small fragments. The various fractures of the cast steel did not exhibit any imperfections, to which the bursting of the gun could have been ascribed. The metal was very uniform, compact, and hard. A fragment was selected for analysis, and furnished the following results:—

One hundred parts contained—

| | |
|-------------------------|--------------|
| Iron | 98·05 |
| Combined carbon . . . | 1·18 |
| Silicium | 0·33 |
| Phosphorus | 0·02 |
| Manganese | <i>trace</i> |
| Cobalt and Nickel . . . | 0·12 |
| Copper | 0·30 |

No sulphur was detected.

The specific gravity of the specimen analysed was found to be 7·836.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.

BY HENRY WATTS, B.A., F.C.S.

On Insolinic Acid.*

By A. W. Hofmann.

ON attempting to purify crude cuminic acid, by boiling it with a mixture of sulphuric acid and bichromate of potassium, it was observed that the cuminic acid is gradually transformed into a new acid, for which I would propose the provisional name of *insolinic acid*.

If one part of cuminic acid be boiled with 8 parts of concentrated sulphuric acid and 12 parts of water, care being taken to condense that which is volatilized, (viz., cuminic acid and water,) and to return it to the seat of the reaction by means of a long upright tube, connected with the flask, the transformation is accomplished in about 12 hours. The crystals of cuminic acid deposited in the neck of the flask and in the condenser-tube at the commencement of the operation disappear; and, after cooling, there will be found floating upon the green liquid a white flour-like powder (insolinic acid). This liquid also retains in suspension a greenish, half-fused mass (insolinate of chromium). The liquid is now filtered, the insoluble mixture washed with water, in order to remove the soluble chromium-salt, and the residue boiled with ammonia; insoluble sesquioxide of chromium is then separated, insolinic acid passing into solution. The ammoniacal solution, on saturation with hydrochloric acid, furnishes a white powder, which, when repeatedly boiled with water, or heated with boiling alcohol (for the purpose of removing any adhering cuminic acid), constitutes pure insolinic acid.

This substance is a white powder, tasteless and inodorous, and apparently without crystalline structure; it appears crystalline, however, under the microscope. Insolinic acid is scarcely dissolved by water; it is almost insoluble in alcohol, and perfectly insoluble in ether. From an aqueous solution, saturated when hot (which possesses a distinctly acid reaction), it is deposited on cooling in

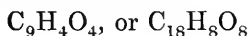
* Ann. Ch. Pharm. xcviij., 197.

the form of a powder, consisting of extremely minute crystals. Insolinic acid is readily dissolved by the fixed alkalies, and also by ammonia, which it perfectly neutralizes. When boiled with the alkaline carbonates, it expels their carbonic acid. It is insoluble in concentrated sulphuric acid, and the solution may be heated without becoming black; on addition of water, the acid is reprecipitated unchanged; no effect results from continued ebullition with the strongest acid. Insolinic acid fuses only at a very high temperature; its fusing point and boiling point nearly coincide. Submitted to distillation, a portion of the acid sublimes unaltered, another portion is decomposed with formation of benzoic acid and benzol, carbonic acid being evolved, and a residue of carbon remaining in the retort.

Combustion of insolinic acid has furnished the following results:

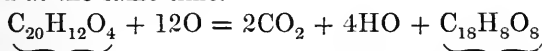
| | | | |
|------|--------------------|---------------------|-------------|
| I. | 0.233 grm. of acid | 0.511 carbonic acid | 0.087 water |
| II. | 0.3325 " | 0.724 " | 0.130 |
| III. | 0.3005 " | 0.6603 " | 0.120 |

These numbers lead to the formula



| Theory. | | Experiment. | | | |
|-------------------|--------------|-------------|-------|-------|-------|
| | | I. | II. | III. | Mean. |
| $\text{C}_{18} =$ | 108 60.00 | 59.82 | 59.37 | 59.92 | 59.70 |
| $\text{H}_8 =$ | 8 4.44 | 4.14 | 4.34 | 4.43 | 4.30 |
| $\text{O}_8 =$ | 64 35.56 | — | — | — | — |
| <hr/> | | | | | |
| | 180 100.00 | | | | |

Hence follows that the new acid is derived from cuminic acid by the partial oxidation of its carbon and hydrogen, oxygen being fixed at the same time.



Cuminic acid.

Insolinic acid.

The evolution of carbonic acid is readily demonstrated by experiment.

The formula $\text{C}_{18}\text{H}_8\text{O}_8$ has been confirmed by the analysis of several salts.

Silver-Salt.—This is separated in the form of a white amorphous curdy precipitate, on decomposing the ammonia salt by nitrate of silver. It requires long continued washing, together with careful exclusion of light. A combustion and several silver-determinations furnished the following results:

| | | | |
|------|-------------------------|---------------------------|---------------------------------|
| I. | 0.3350 grm. silver-salt | 0.3348 carb. acid | 0.0455 water, and 0.1835 silver |
| II. | 0.3455 " | 0.1891 silver | |
| III. | 0.4157 " | 0.2274 " | |
| IV. | 0.3233 " | 0.1778 " | |
| V. | 0.3030 " | 0.4380 " | |
| VI. | 0.9710 " | 0.7027 chloride of silver | |
| VII. | 0.1910 " | 0.1380 " | |

These analytical results lead to the formula



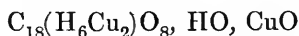
| Theory. | | | Experiment. | | | | | | | |
|-----------------|-------|-------|-------------|-------|-------|-------|-------|-------|-------|-------|
| | | | I. | II. | III. | IV. | V. | VI. | VII. | Mean. |
| C_{18} | . 108 | 27.41 | 27.25 | — | — | — | — | — | — | 27.25 |
| H_6 | . 6 | 1.52 | 1.507 | — | — | — | — | — | — | 1.507 |
| Ag_2 | . 216 | 54.82 | 54.77 | 54.73 | 54.70 | 54.99 | 54.54 | 54.46 | 54.34 | 54.64 |
| O_8 | . 64 | 16.25 | — | — | — | — | — | — | — | — |
| 390 100.00 | | | | | | | | | | |

Silver-determination VII., relates to a salt, the acid of which had been boiled for eight days with the oxidizing mixture, a proof that insolinic acid is not further changed in this manner. In this analysis, the acid which was separated on addition of nitric acid was likewise collected and weighed. 0.191 grm. silver-salt furnished 0.0865 grm. = 45.28 per cent. of acid, whilst 46.15 per cent. should have been obtained.

Copper-Salt.—A light blue salt, which is precipitated on mixing a neutral solution of insolinic acid with sulphate of copper. Analysis furnishes the following numbers:

| | | |
|-----|--------------------|------------------------|
| I. | 0.7805 copper salt | 0.3185 oxide of copper |
| II. | 0.7085 „ | 0.2885 „ |

according to which the precipitate appears to be a basic compound, probably

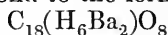


| | | Experiment. | |
|---------|-------|-------------|-------|
| Theory. | | I. | II. |
| Copper | 32.78 | 32.58 | 32.55 |

Barium-Salt.—Dilute solutions of insolinate of ammonium are not precipitated by salts of barium; on mixing concentrated solutions, a white, more or less crystalline, precipitate is produced, which may be washed with cold water. For analysis, the salt was dried at between 120° and 130° C, the barium was estimated as carbonate, and in one case as sulphate.

| | | |
|------|--------------------|----------------------------|
| I. | 0.4290 barium-salt | 0.2700 carbonate of barium |
| II. | 0.2760 „ | 0.1728 „ |
| III. | 0.4045 „ | 0.2545 „ |
| IV. | 0.5210 „ | 0.3280 „ |
| V. | 0.6920 „ | 0.5115 sulphate of barium. |

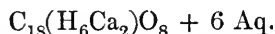
These numbers correspond to the formula —



| Theory. | | | Experiment. | | | | | |
|-----------------|-------|-------|-------------|-------|-------|-------|-------|-------|
| | | | I. | II. | III. | IV. | V. | Mean. |
| C_{18} | . 108 | 34.28 | — | — | — | — | — | — |
| H_6 | . 6 | 1.90 | — | — | — | — | — | — |
| Ba_2 | . 137 | 43.49 | 43.79 | 43.51 | 43.73 | 43.78 | 43.45 | 43.65 |
| O_8 | . 64 | 20.33 | — | — | — | — | — | — |
| 315 100.00 | | | | | | | | |

In a further analysis, VI., 0.356 barium-salt were decomposed by hydrochloric acid and the separated insolinic acid collected. It amounted to 0.2020 grm. = 56.74 per cent., whilst 57.14 per cent. of acid should have been obtained.

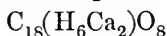
Calcium-Salt.—This is obtained as the barium-salt, which it also much resembles in its physical properties. When dried at 100° C, it contains—



| | | | | |
|------|-------|--------------|--------|----------------------|
| I. | 0.504 | calcium-salt | 0.1870 | carbonate of calcium |
| II. | 0.436 | „ | 0.1645 | „ „ |
| III. | 1.005 | „ | 0.2000 | „ „ |

| Theory. | | | | Experiment. | | | |
|-----------------|-----|-----|-------|-------------|-------|-------|-------|
| | | | | I. | II. | III. | Mean. |
| C_{18} | . . | 108 | 39.70 | — | — | — | — |
| H_6 | . . | 6 | 2.20 | — | — | — | — |
| Ca_2 | . . | 40 | 14.70 | 14.84 | 15.08 | — | 14.96 |
| O_8 | . . | 64 | 23.60 | — | — | — | — |
| 6 HO. | . . | 54 | 19.80 | — | — | 19.90 | 19.90 |
| <hr/> | | | | | | | |
| 272 100.00 | | | | | | | |

The water escapes between 120° and 130° C; when dried at this temperature, the salt has the composition



as demonstrated by the following determination :

0.800 salt gave 0.3735 carbonate of calcium.

| Theory. | | | | Experiment. |
|-----------------|-----|-----|-------|-------------|
| C_{18} | . . | 108 | 49.54 | — |
| H_6 | . . | 6 | 2.75 | — |
| Ca_2 | . . | 40 | 18.35 | 18.67 |
| O_8 | . . | 64 | 29.36 | — |
| <hr/> | | | | |
| 218 100.00 | | | | |

Potassium-Salts.—Of these there are two, one neutral and one acid.

(a.) *Neutral Potassium-Salt.*—This is precipitated as a crystalline powder, upon mixing the saturated solution of insolinic acid in aqueous potassa, with strong spirits of wine. When dry, the salt exhibits a remarkable satiny lustre.

Analysis furnished the following results :

| | | | | | |
|------|--------|----------------|------|-------|------------------------------|
| I. | 0.5280 | potassium salt | gave | 1.002 | potassiochloride of platinum |
| II. | 0.3176 | „ „ | | 0.220 | acid |
| III. | 0.5280 | „ „ | | 0.366 | „ |

The formula



requires the following values :

| Theory. | | | | Experiment. |
|-----------------|---|-----|--------|-------------|
| | | | | I. |
| C_{18} | . | 108 | 42.19 | — |
| H_6 | . | 6 | 2.34 | — |
| K_2 | . | 78 | 30.46 | 30.36 |
| O_8 | . | 64 | 25.01 | — |
| | | 256 | 100.00 | |

Percentage of acid corresponding to the neutral potassium-salt :

| Theory. | Experiment. | |
|---------|-------------|-------|
| | II. | III. |
| 70.31 | 69.27 | 69.30 |

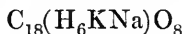
(b.) *Acid Potassium-Salt*.—This is formed by boiling the solution of the neutral salt with an excess of insolinic acid ; from the hot filtered solution there separate, on cooling, small crystalline scales, which contain



I have made a determination of the acid only. 0.4025 of the acid salt gave 0.3305 acid ; percentage of acid corresponding to the acid potassium salt :

| Theory. | Experiment. |
|---------|-------------|
| 82.56 | 82.11 |

Potassium-Sodium-Salt.—I have endeavoured to obtain additional evidence of the bibasic nature of insolinic acid, by producing a compound which should contain the two alkali-metals. On precipitating the solution of the acid potassium-salt with carbonate of sodium, a salt is thrown down, the analysis of which has actually led to the formula



0.1955 potassium-sodium-salt gave 0.1985 potassiochloride of platinum.

| Theory. | | | | Experiment. |
|-----------------|---|-----|--------|-------------|
| C_{18} | . | 108 | 45.00 | — |
| H_6 | . | 6 | 2.50 | — |
| K | . | 39 | 16.25 | 16.16 |
| Na | . | 23 | 9.58 | — |
| O_8 | . | 64 | 26.67 | — |
| | | 240 | 100.00 | |

In the above potassium-determination, the insolinic acid, separated on addition of hydrochloric acid, was likewise collected.

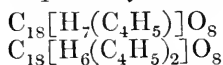
0.1955 salt furnished 0.1456 acid.

Percentage of acid corresponding to the potassium-sodium-salt :

| Theory. | Experiment. |
|---------|-------------|
| 75.0 | 74.47 |

Unfortunately it is not possible to obtain the preceding compound by crystallization ; it might, therefore, be nothing but a mechanical mixture of the neutral potassium-salt and the neutral sodium-salt. Too much argumentative value must not therefore be attached to the analysis of this compound.

Under these circumstances, the study of insolinic ethers would be possessed of a special interest. The formation, however, of these ethers can only be accomplished with the greatest difficulty, in consequence of the insolubility of the acid. They were actually obtained by the action of iodide of ethyl on the silver-salt in sealed tubes, and likewise by treating the acid suspended in alcohol with hydrochloric acid, but not in quantity sufficient to admit of careful study. I can only affirm that there exist two ether-compounds, the one possessing acid properties, the other neutral ; both may be separated by potassa, and probably contain



I have, however, no analytical evidence to offer for this assumption.

The following table comprises all the compounds of insolinic acid which have been analyzed :

| | | | |
|---------------------------------|-----------------|-----------------------------|-----------------------------------|
| Acid | C_{18} | H_8 | O_8 |
| Silver-salt | C_{18} | $(\text{H}_6 \text{ Ag}_2)$ | O_8 |
| Copper-salt | C_{18} | $(\text{H}_6 \text{ Cu}_2)$ | $\text{O}_8 + \text{HO, CuO (?)}$ |
| Barium-salt | C_{18} | $(\text{H}_6 \text{ Ba}_2)$ | O_8 |
| Calcium-salt— | | | |
| at 100° C | C_{18} | $(\text{H}_6 \text{ Ca}_2)$ | $\text{O}_8 + 6 \text{ HO}$ |
| at 130° C | C_{18} | $(\text{H}_6 \text{ Ca}_2)$ | O_8 |
| Potassium-salt— | | | |
| neutral. | C_{18} | $(\text{H}_6 \text{ K}_2)$ | O_8 |
| acid | C_{18} | $(\text{H}_7 \text{ K})$ | O_8 |
| Potassium-sodium-salt | C_{18} | $(\text{H}_6 \text{ K Na})$ | O_8 |

It now only remained to examine the behaviour of insolinic acid and its compounds under the influence of heat. On rapidly heating these substances, an aromatic odour is evolved, strongly reminding one of benzoic compounds. In fact, benzoic acid and benzole are found in greater or less quantity among the distillation-products of insolinic acid. When an intimate mixture of insolinic acid and pumice stone is distilled rapidly over a naked flame, and the semi-crystalline deposit condensed in the neck of the retort is heated with boiling water, benzoic acid in rather considerable

quantities is dissolved, and crystallizes on cooling. The residue is insolinic acid, which has distilled unchanged. The nature of both substances was fixed by a number; that of benzoic acid by the determination of the silver in the silver-salt.

0.242 grm. silver salt gave 0.1188 silver.

Percentage of silver in benzoate of silver:

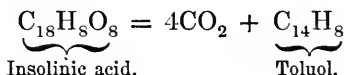
| $C_{14}(H_5Ag)O_4$ | |
|--------------------|-------------|
| Theory. | Experiment. |
| 47.1 | 47.0 |

Insolinic acid was identified by the analysis of the barium-salt. In fact, determination VI., in the preceding analysis of the barium compound, refers to salt prepared with the sublimed acid.

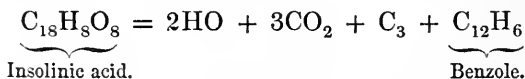
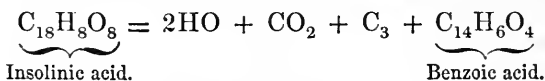
On distilling a mixture of insolinic acid and caustic baryta, a transparent liquid passes over, carbonate of barium mixed with charcoal remaining in the retort. The liquid was identified as pure benzol, both by the determination of the boiling point and by its transformation into nitrobenzole and aniline.

The conversion of insolinic acid into benzol was effected on a rather extensive scale, for, in fact, I was by no means prepared for this metamorphosis.

Considerations to which I shall have to revert at the conclusion of this note, had led me to expect the production of toluol ($C_{14}H_8$) according to the equation—



Careful and repeated experiments have, however, satisfied me that insolinic acid does not furnish a trace of toluol under these circumstances. The molecule of the acid experiences a more profoundly pervading change, as is evident from the separation of the carbon. The transformation of insolinic acid into benzoic acid and benzol may be exhibited by the following equations—



The formation of insolinic acid from cuminic acid led to the examination of some allied bodies in the same direction.

Nitrocuminic acid, boiled for several days with chromate of potassium and sulphuric acid, did not exhibit the slightest alteration. The homologous benzoic acid was not attacked by the oxidising mixture, even after having been boiled with it for weeks. Toluylic acid,

standing, as it does, between benzoic and cuminic acid, appeared to promise a different result. Toluyllic acid was, as is well known, produced by Noad, on submitting cymol (the hydro-carbon accompanying the aldehyde of cuminic acid in Roman cumin oil) to dilute nitric acid. The preparation of toluyllic acid, by means of nitric acid, is, however, an extremely irksome and tedious operation. It is necessary to employ the nitric acid so extremely dilute as hardly to act on the hydrocarbon; otherwise, nitrotoluyllic acid only is obtained. I had hoped to arrive at a more rapid result by the action of the chromic oxidising mixture. In fact, cymol is energetically attacked by this mixture; but the acid which is formed is not toluyllic, but insolinic acid,—the same acid which was produced from cuminic acid.* Determination III. and IV., to be found in the analysis of insolinate of barium, refer to salts obtained from insolinic acid prepared from cymol. This observation indicates a simple method of easily procuring insolinic acid in considerable quantity. It is only necessary to heat the ordinary Roman cumin-oil (cymol and cuminol), with a mixture of chromate of potassium and sulphuric acid. It is, however, necessary to apply the heat very slowly, and to be provided with the means of cooling rapidly, otherwise much oil may be lost, in consequence of the extraordinary energy of the action.

The preceding researches suggested some additional experiments, the results of which I will here briefly mention.

When cumol is boiled for some time, with a mixture of sulphuric acid and chromate of potassium, it is readily and completely converted into benzoic acid, exhibiting, under these circumstances, the same behaviour which is observed on heating it with dilute nitric acid.

The oxidation-products of toluol have already been examined by Deville,† who found that this hydrocarbon is likewise converted into benzoic acid. But this chemist succeeded only once in obtaining benzoic acid from toluol; and, since the toluol he employed was procured from balsam of tolu, which, as is well known, furnishes a considerable quantity of benzoic acid, he did not regard the experiment as conclusive. I have, therefore, repeated the experiment with toluol prepared from coal-gas naphtha. The action of the oxidizing mixture is slow; but the transformation was repeatedly and easily effected. The identity of the benzoic acid obtained by this method was fixed by a number.

0.251 silver salt left 0.1175

Percentage of silver in benzoate of silver:

| $C_{14}(H_5Ag)O_4$ | |
|--------------------|-------------|
| Theory. | Experiment. |
| 47.1 | 46.8 |

* It is conceivable that in a first stage of this reaction the toluyllic acid is actually formed. I have not varied the experiment sufficiently to offer a decided opinion on this subject.

† Ann. Ch. Phys. [3], III. 171.

When considered by itself, insolinic acid has but slight claims on the attention of chemists; but when viewed in connection with other groups of bodies, it acquires increased interest. Some years since, Gerhardt pointed out, that to the homologous series of *monobasic fatty acids*, $C_{2n}H_{2n}O_4$, the lowest terms of which are formic and acetic acid, there runs parallel a homologous series of bibasic acids $C_{2n}H_{2n-2}O_8$, the simplest member of which is oxalic acid. These two series of acids are connected by the closest ties, and very conclusive experiments have demonstrated that the members of the former may be easily converted into those of the latter. Such is the case of the transformation of butyric into succinic acid, effected by M. Dessaignes, by means of oxidizing agents.

The following table exhibits these two series of acids arranged according to their carbon :

| | | | |
|-----------------|-------------------|-------------------|-------------------|
| Formic acid | $C_2H_2O_4$ | — | |
| Acetic acid | $C_4H_4O_4$ | Oxalic acid | $C_4H_2O_8$ |
| Propionic acid | $C_6H_6O_4$ | — ? | $C_6H_4O_8$ |
| Butyric acid | $C_8H_8O_4$ | Succinic acid | $C_8H_6O_8$ |
| Valeric acid | $C_{10}H_{10}O_4$ | Pyrotartaric acid | $C_{10}H_8O_8$ |
| Caproic acid | $C_{12}H_{12}O_4$ | Adipic acid | $C_{12}H_{10}O_8$ |
| Enanthylic acid | $C_{14}H_{14}O_4$ | Pimelic acid | $C_{14}H_{12}O_8$ |
| Caprylic acid | $C_{16}H_{16}O_4$ | Suberic acid | $C_{16}H_{14}O_8$ |
| Pelargonic acid | $C_{18}H_{18}O_4$ | — ? | $C_{18}H_{16}O_8$ |
| Rutic acid | $C_{20}H_{20}O_4$ | Sebacic acid | $C_{20}H_{18}O_8$ |

The existence and the mode of formation of insolinic acid prove that to the series of *monobasic aromatic acids*, $C_nH_{n-8}O_4$, the lowest term of which is benzoic acid, there corresponds likewise a series of bibasic acids, $C_{2n}H_{2n-8-2}O_8 = C_{2n}H_{2n-10}O_8$. Of this series few members are at present known; but the group of aromatic acids is itself very imperfect and limited. The two series comprise at present the following terms :

| | | | |
|---------------|-------------------|-------------------|-------------------|
| Benzoic acid | $C_{14}H_6O_4$ | ? | $C_{14}H_4O_8$ |
| Toluolic acid | $C_{16}H_8O_4$ | Terephthalic acid | } $C_{16}H_6O_8$ |
| ? | $C_{18}H_{10}O_4$ | Phthalic acid | |
| Cuminic acid | $C_{20}H_{12}O_4$ | Insolinic acid | $C_{18}H_8O_8$ |
| | | ? | $C_{20}H_{10}O_8$ |

It is evident that the carbon being made the standard of comparison, the bibasic insolinic acid corresponds to the monobasic acid, which stands between toluylic and cuminic acid, and which is at present unknown.*

In addition to this unknown acid, toluylic acid is represented in the series of bibasic acids. There are, in fact, two bodies which

* Benzo-glycolic acid, formed by the action of nitrous acid on hippuric acid, has the same composition as insolinic acid; but it is monobasic, and differs, moreover, from insolinic acid by its physical properties.

may be regarded as representations of toluylic acid. These are phthalic acid, and a compound which Caillot* produced by oxidizing oil of turpentin by means of nitric acid, and which he has described under the name of terephthalic acid.† Both acids contain $C_{16}H_6O_8$; both are bibasic; both are decomposed under the influence of heat, or, more perfectly by heating with baryta, into carbonic acid and benzol. But, notwithstanding this similarity, both are positively distinct chemical substances; for, while phthalic acid is soluble in water and alcohol, and may be obtained from these liquids in definite crystals, terephthalic acid is scarcely attacked by these solvents, and forms at best an indistinctly crystalline powder. Moreover, phthalic acid, like the bibasic acids, corresponding to the series $C_{2n}H_{2n}O_4$, loses two equivalents of water when submitted to the action of heat, easily forms amidogen-compounds, and may without difficulty be converted into a nitro-substitute. All these properties are absent in terephthalic acid. I have here purposely compared the properties of these two acids, in order to show that terephthalic acid in its entire deportment resembles closely insolinic acid; whilst phthalic acid, in its behaviour, solubility, crystallization, dehydratability, and power of forming amidogen-compounds, approaches nearer the bibasic acids of the series which runs parallel with the fatty acids. It is conceivable that phthalic acid is the true representative in the series of bibasic aromatic acids ($C_{2n}H_{2n-10}O_8$), and that the homologues, terephthalic, and insolinic acids have to be viewed as acids isomeric with the members of the former series, whose analogues for the bibasic fatty acids are not yet discovered.

* Ann. Chem. Phys. [3], xxi. 30.

† Caillot's memoir on oil of turpentine was published ten years since, and obviously contains several statements which require confirmation. I therefore thought it desirable to repeat these experiments, so far at least as they related to terephthalic acid. By following exactly the method indicated by Caillot, a small quantity of an insoluble, somewhat coloured, acid was ultimately obtained, the barium- and silver-salts of which resembled the corresponding compounds of insolinic acid. On analysis, these salts furnished numbers representing pretty accurately terephthalic acid.

0·263 barium salt; 0·2024 sulphate of barium



| | Theory. | Experiment. |
|--------|---------|-------------|
| Barium | 45·51 | 45·24 |

0·190 silver salt; 0·1073 silver



| | Theory. | Experiment. |
|--------|---------|-------------|
| Silver | 56·84 | 56·46. |

On Lophine.*

By A. Gössmann and E. Atkinson.

AMONG the products of decomposition formed by heating hydrobenzamide to a high temperature, Laurent† found, besides amarone, a new base, to which he gave the name lophine. At first he proposed for it the formula $C_{46}H_{17}N_2$, and afterwards $C_{46}H_{16}N_2$.

About the same time, Fownes obtained, by the dry distillation of amarine (the benzoline of Fownes), a substance possessing weak basic properties, to which he gave the name pyrobenzoline, and the composition of which he expressed by the formula $C_{21}H_8N$.

It was observed by one of us‡ that lophine was formed when the compound of bisulphite of ammonia with oil of bitter almonds is heated with dry hydrate of lime. This led us to examine the base, on the one hand with a view to establish its true formula, and on the other to ascertain if any connection existed between the lophine of Laurent and the pyrobenzoline of Fownes.

The results of our investigation determine us to adopt for lophine the formula $C_{42}H_{17}N_2$; and have further led us to the conviction that pyrobenzoline is identical with lophine.

In the paper above cited, which describes the formation of lophine and amarine from the compound of oil of bitter almonds and bisulphite of ammonia, it was mentioned that the formation of lophine was greatly promoted by rapidly heating the mixture to a temperature of 250° to $300^\circ C$. It being our object to obtain as large a product of lophine as possible, we endeavoured to ascertain the conditions for the fulfilment of this object. We found that by mixing with the hydrate of lime its weight of caustic lime, and by covering the retort as far as it was filled with the mixture, with live coals, from the beginning of the operation, the greatest product was obtained. An apparatus constructed as follows proved very convenient. A shallowish globular retort was coated with clay, to about the height to which the fire was to be piled up. The neck of the retort, cut off to six inches in length, was inserted in a tubulated cylinder, which served as a receiver. In the tubulure of the cylinder a tube bent twice at right angles was inserted, the other end of which dipped into water. In this manner it was possible to observe the occurrence of any volatile oily products as well as gases. The greatest products were

* Ann. Ch. Pharm. xcvii, 283.

† Revue Scientifique, No. 56; J. pr. Chem., xxxv., 455.

‡ Ann. Ch. Pharm., xciii., 331.

obtained when small quantities were operated upon; 10 to 15 grammes of the oil of bitter almonds compound with about four to six times the quantity of the lime mixture appeared to be the best proportions for one operation. If the operation be conducted as above indicated, only a small quantity of amarine is formed at first. When this has melted down, the upper part of the retort begins to be covered with radiant masses of lophine, the formation of secondary products ceases, and there seems only to be formed, besides lophine, some free ammonia. At the beginning, a small quantity of an aromatic oily product accompanies the lophine. But this only appeared to result from amarine, which, at the beginning of the operation, had settled in the upper part of the retort, and which, by the rapidly increased heat, had been decomposed into lophine and some products which have not been closely examined. Of these, the principal appears to be *amarone*. This body, described by Laurent, is only distinguished from lophine by its differing solubility in ether and alcohol, but contains 88.4 p.c. of carbon. It is apparently to the presence of small quantities of this substance, that the conflicting analyses of lophine must be ascribed. We have the more reason to ascribe these discrepancies to this cause, inasmuch as different preparations of lophine obtained by the above process, in which the occurrence of secondary products is reduced to a minimum, and purified as follows, gave us well agreeing analytical results.

The lophine which we used for analysis and for the preparation of the various salts was thus purified. In order to free the crude product of distillation from adhering amarine and oily and colouring admixtures, it was digested several times with moderately strong alcohol. It was then dissolved in boiling alcohol, to separate any lime which might have been mechanically carried over, boiled for some time with animal charcoal, and filtered. On standing, tuft-shaped masses of long needles separated out, and the mother liquid was evaporated as long as any of these were formed. These crystals, separated from the mother-liquors, were dissolved in alcohol acidulated with hydrochloric acid, the solution precipitated boiling by aqueous ammonia, and the base repeatedly crystallized from alcohol.

The base thus purified exhibited the following properties. From an alcoholic solution it crystallizes in tufted-grouped needles often an inch long, and possessing a lustre similar to that of caffenin. The crystals, which at first are transparent, become opalescent, but retain their lustre. The crystals are tasteless and inodorous; scarcely exhibit any alkaline reaction; are difficultly soluble in ether, more so in alcohol, and very little in water. Heated to 250° C. they sublime gradually without leaving any residue, and without melting. They melt at 265° C. to a clear transparent mass, which at 260° C. solidifies to a

radiating crystalline mass. They sublime in a form similar to that of benzoic acid.

The alcoholic solution of the base, and particularly of the sulphate and hydrochlorate, exhibit the phenomenon of fluorescence similarly to quinine, though not in so high a degree. But, unlike that base, lophine effects no rotation of the plane of polarization.

The analyses of lophine purified as above, and of various preparations, gave the following numbers:

| | | | | | | | |
|------|--------|--|--------|-----------------|-----|--------|----|
| I. | 0.2966 | gave | 0.9225 | CO ₂ | and | 0.152 | HO |
| II. | 0.2610 | „ | 0.8107 | CO ₂ | „ | 0.1327 | HO |
| III. | 0.2396 | „ | 0.7445 | CO ₂ | „ | 0.1250 | HO |
| IV. | 0.2449 | „ | 0.7606 | CO ₂ | „ | 0.1245 | HO |
| V. | 0.3235 | „ | 1.0031 | CO ₂ | „ | 0.1630 | HO |
| VI. | 0.2325 | „ | — | — | „ | 0.1188 | HO |
| VII. | 0.343 | afforded on treatment with soda-lime, &c., | | | | | |
| | | 0.5184 NH ₄ Cl + Pt Cl ₂ . | | | | | |

The formula hitherto proposed, partly on analytical data and partly on theoretical grounds, are as follows:

| I. Laurent. | II. Laurent. | Fownes. | List (Gmelin's Handbuch, vi. 157). |
|--|--|----------------------------------|--|
| C ₄₆ H ₁₇ N ₂ | C ₄₆ H ₁₆ N ₂ | C ₂₁ H ₈ N | C ₄₄ H ₁₆ N ₂ |
| C 85.98 | 86.25 | 85.13 | 85.75 |
| H 5.29 | 5.00 | 5.41 | 5.19 |
| N 8.72 | 8.75 | 9.46 | 9.09 |

We propose the formula C₄₂H₁₇N₂, and subjoin the calculated analytical results:

| Calculated. | | Found. | | | | | | | Mean. |
|-----------------|-------|--------|-------|-------|-------|-------|------|------|-------|
| | | I. | II. | III. | IV. | V. | VI. | VII. | |
| C ₄₂ | 84.84 | 84.82 | 84.71 | 84.74 | 84.84 | 84.56 | — | — | 84.73 |
| H ₁₇ | 5.72 | 5.69 | 5.65 | 5.79 | 5.35 | 5.60 | 5.70 | — | 5.63 |
| N ₂ | 9.42 | — | — | — | — | — | — | 9.47 | 9.47 |

The carbon, which has most influence on the formula, agrees best with our analyses. In order to ensure complete combustion, we used tubes six inches longer than is usual in combustion with oxide of copper and oxygen. To prevent the formation of any oxides of nitrogen, sheet copper was placed at the anterior part of the tube.

The identity of the pyrobenzoline of Fownes with the lophine of Laurent has been already suggested by Gerhardt.* And, indeed, after Bertagnini† had shown that hydrobenzamide could be converted into amarine by simply heating it, there could be little doubt about it. A direct proof only was needed. Our observations of the properties of lophine, as detailed above, agree perfectly with Fownes's description of pyrobenzoline. And the

* *Traité de Chimie Organique*, tome iii., 179.

† *Liebig's Annalen*.

analyses of this chemist agree well with our own. As he did not examine the nature of the base more closely, he could only give as a formula the simplest expression of his analytical results. On doubling his formula, it only differs by one equivalent of hydrogen from our own.

Lophine is a very weak base, and has scarcely any alkaline reaction. It forms, indeed, well characterised salts, but these have a tendency, on recrystallization, to give up part of their acid, and become changed into basic compounds. This is particularly the case with the sulphate.

Hydrochlorate of Lophine = $C_{42}H_{17}N_2 + HCl + HO$. If to a hot saturated alcoholic solution of lophine, hydrochloric acid be added till the mixture is decidedly acid, the hydrochlorate separates out, on cooling, in large transparent needles, very similar to pure lophine. If these crystals be allowed to stand for some time in the acid mother-liquor, they change into small, white, opaque prisms. We have observed this to be the case with several lophine compounds. It is possible that the change depends on some loss of water, for we could ascertain no essential difference in the comportment of this form of the salt. If the base be treated directly with concentrated hydrochloric acid, it becomes resinous, and can only be obtained in the crystalline state by removing the excess of acid, and recrystallization from alcohol.

The hydrochlorate has a feebly acid reaction. It is more soluble in alcohol and water, and shows the fluorescent appearance more strongly than the pure base.

The analyses afforded the following results :

| | | | | | | | |
|------|--------|------|--------|--------|-----|--------|----|
| I. | 0.272 | gave | 0.736 | CO_2 | and | 0.1355 | HO |
| II. | 0.1984 | „ | 0.538 | CO_2 | „ | 0.1010 | HO |
| III. | 0.2184 | „ | 0.0834 | Ag | Cl. | | |

| Calculated. | | Found. | | |
|-------------|------------|--------|-------|------|
| | | I. | II. | III. |
| C | 42 = 73.57 | 73.78 | 73.80 | — |
| H | 19 = 5.54 | 5.51 | 5.65 | — |
| N | 2 = 8.17 | — | — | — |
| Cl | 1 = 10.36 | — | — | 9.42 |
| O | 1 = 2.33 | | | |

Hydriodate of Lophine, $C_{42}H_{17}N_2 + HI$. This salt is obtained in the same manner as the hydrochlorate. It crystallizes easily in large needles, which are more soluble in alcohol and ether than the hydrochlorate. It crystallizes from a very acid solution in granular crystals. Hydriodate of lophine is very soluble in iodide of ethyl. Its other properties are exactly similar to those of the hydrochlorate.

Sulphate of Lophine, $C_{42}H_{17}N_2 + HO, SO_3$? When a solution of lophine, to which excess of sulphuric acid has been added, is

allowed to evaporate slowly, the sulphate separates out in the form of broad, transparent, rhombic tables, which are often 4 or 5 lines in length and 2 lines in breadth. On standing in the air, they become opaque and effloresce. When crystallized more rapidly, the compound separates out in the form of large needles, which, on standing some time in the acid mother-liquor, change into small white opaque needles. At each recrystallization from alcohol, the salt becomes more basic, a phenomenon which appears to have been observed by Laurent; at least, some of his analyses allow of this assumption. By frequent solution and recrystallization from water, the sulphuric acid may be almost entirely removed from the compound, as our analyses have convinced us. The analytical results which we have obtained exhibit, from this reason, great variation, and we have not thought it necessary to adduce them.

Nitrate of Lophine, $C_{42}H_{17}N_2 + HO, NO_5$. This salt crystallizes from a concentrated alcoholic solution of lophine, which has been acidulated with nitric acid, in the form of small plates. If these be covered with concentrated nitric acid which is free from nitrous acid, they become converted into an oily mass. In other particulars we can confirm Laurent's description of this salt.

Hydrochlorate of Lophine and Bichloride of Platinum, $C_{42}H_{17}N_2 HCl + Pt Cl_2$. This double salt is formed on mixing a dilute alcoholic solution of bichloride of platinum with a warm moderately concentrated solution of lophine containing excess of hydrochloric acid. On cooling, crystals which are often needle-shaped separate out, and these, on standing, sometimes crumble to a beautiful orange-yellow crystalline powder. This salt is more soluble in alcohol than any other compound of lophine. If an alcoholic solution of lophine be heated some time with excess of bichloride of platinum, the base becomes essentially altered. Platinum is separated in a very finely divided state, and the liquid filtered off from this is very difficult to crystallize. The body which separates out is generally soft, adhering together in a resinous mass, and the quantity of platinum in it is less than in the crystallized double salt. The analysis of the double salt gave us the following numbers:

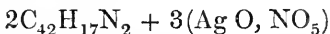
- I. 0.3280 gave 0.5920 CO_2 and 0.116 HO
 II. 0.2250 „ 0.0445 Platinum.

| Calculated. | | Found. | |
|-------------|-------|--------|-------|
| | | I. | II. |
| C_{42} | 50.08 | 49.22 | — |
| H_{18} | 3.58 | 3.93 | — |
| N_2 | 5.56 | — | — |
| Cl_3 | 21.16 | — | — |
| Pt_1 | 19.61 | — | 19.77 |

Bichloride of platinum unites also directly with lophine. When a concentrated alcoholic solution of lophine is mixed with a concentrated, neutral, alcoholic solution of bichloride of platinum, a clear, orange-yellow, microscopic crystalline compound separates, which seems to be a compound of $4(C_{42}H_{17}N_2) + 3PtCl_2$. A compound thus constituted would require 17.45 per cent. of platinum; our analyses give the following numbers:

| | | | | | |
|------|--------|------|--------|------------|-----------|
| I. | 0.3450 | gave | 0.0605 | Pt = 17.53 | per cent. |
| II. | 0.2540 | „ | 0.0504 | Pt = 17.27 | „ |
| III. | 0.3515 | „ | 0.0610 | Pt = 17.35 | „ |

Lophine and Nitrate of Silver.—If a neutral, moderately concentrated, alcoholic solution of nitrate of silver be mixed with a hot, saturated, alcoholic solution of lophine, the mixture solidifies on cooling to a mass of crystals. If these be dissolved in cold alcohol, and left to spontaneous evaporation, the compound separates in tolerably large white needles, which on analysis gave numbers corresponding to the above formula. But on attempting to purify the compound by recrystallization, it changes by boiling into a pulverulent, crystalline, difficultly soluble substance, which settles down with a somewhat violet tint. This compound is thus constituted:

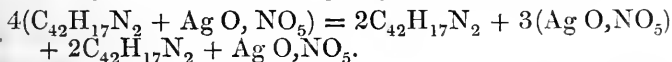


0.2295 gave 0.0666 Ag = 29.01 per cent. The above formula requires 29.36 per cent. After separating this body, and further evaporation of the mother-liquor, another and more soluble compound crystallizes out, in brilliant white needles. It has the formula



0.2800 gave 0.039 Ag = 13.92 p.c. The above formula requires 14.14.

The change effected on boiling may be thus expressed:



In order to get a clearer view of the process of the formation of lophine, we endeavoured to ascertain its constitution, and to see to what class of artificial bases it belonged. To this end, various attempts to substitute ethyl were made, by treating it with iodide of ethyl. Pure lophine was enclosed in a glass tube with alcohol and excess of iodide of ethyl, in which it was abundantly soluble, and left for some weeks. Another portion of lophine, which had also been enclosed with iodide of ethyl and alcohol, was heated for three or four days to $100^\circ C.$, and then left to stand some weeks. Both portions were examined separately, but showed the same phenomena. The contents of the tubes had an acid reaction, arising from hydriodic acid. After the excess of iodide

of ethyl had been distilled off, a readily soluble hydriodate separated in fine needles. This was recrystallized from alcohol, and one portion treated with oxide of silver. Another portion was treated with ammonia. In both cases the substances obtained afforded analytical results perfectly agreeing with the composition of pure lophine. Hence, under these circumstances, no substitution had taken place. A portion of the iodide of ethyl had decomposed into alcohol and hydriodic acid, which united with the lophine to form a hydriodate. A similar phenomenon was observed by How,* when narcotine and several other bases were similarly treated.

Examination of select Vegetable Products from India.

By John Stenhouse, L.L.D., F.R.S.

Read before the Royal Society, December 6, 1855.

PART I.

THROUGH the kindness of my esteemed friend Dr. Royle, I have been permitted to select such vegetable products from the extensive collection at the India House as seemed most likely to repay the trouble of investigation. My attention during the last twelve months has been chiefly directed to three of these vegetable substances; and the results of their examination I now take the liberty of submitting to the Royal Society, to be followed by those of the others as they may be completed.

DATISCA CANNABINA.

The first of these substances which I examined consisted of a quantity of the roots of the *Datisca cannabina*, from Lahore, where this plant is employed to dye silk of a fast yellow colour. The roots, which had been cut into pieces about six or eight inches long, were from one-half to three-quarters of an inch in thickness. They had a deep yellow colour. The leaves and smaller branches of the *Datisca cannabina* from the Levant have long been employed for a similar purpose in the south of France. A decoction of the leaves of the *Datisca cannabina* was examined by Braconnot in 1816, who discovered in it a crystallizable principle to which he gave the name of *datiscine*. Braconnot, of course, did not subject this substance to analysis, but he described its appearance and

* Transactions of Edin. Royal Society, 21, 1.

properties in an exceedingly accurate manner.* The observations of Braconnot had fallen into such entire oblivion, however, that for many years past, we find in most of the larger systems of chemistry the term *datiscine* used as synonymous with *inuline*. Thus in Brande's 'Chemistry,' vol. ii. page 1168, we find it stated that a variety of names had been given to inuline, such as "dahline, datiscine," &c. In Löwig's 'Chemistry of Organic Compounds,' vol. i. page 359, the same error is repeated, where, under the article "inuline," the synonyms given are "dahline and datiscine."

The bruised roots were extracted in a Mohr's apparatus by long-continued digestion with wood-spirit. The liquor obtained, which had a dark brown colour, was concentrated by distilling off a portion of the wood-spirit. The brown syrupy liquid remaining in the retort, on being poured into open vessels and standing for some time, deposited a resinous matter containing merely traces of a crystalline substance. When this syrupy liquid, however, was treated with about half its bulk of hot water, the greater portion of the brown resin was rapidly deposited; and the mother-liquor, having been poured off and left to slow spontaneous evaporation, deposited a considerable quantity of an imperfectly crystallizable substance resembling grape-sugar. These crystals are impure *datiscine*, still retaining a considerable amount of resinous matter, to which the dark brown colour is owing.

They may be purified in various ways, advantage being taken of the greater solubility of the resinous matter in alcohol or ether, than that of the *datiscine*. By repeated crystallizations, therefore, from either of these liquids, the *datiscine* may be rendered almost perfectly colourless, the impurities remaining in the mother-liquor. The following is the method which I have found, on the whole, most convenient. The crude *datiscine*, while still moist, is strongly pressed between folds of blotting-paper; it is then dissolved in alcohol, and again treated with water, which throws down the resin. The diluted alcoholic solution, after standing some time, yields the *datiscine* in a much finer state. On repeating this operation several times, the *datiscine* may be obtained perfectly pure. In order to separate any traces of tannic acid which might have been present, I repeatedly added a concentrated solution of gelatine to the alcoholic solution of the *datiscine*, and after careful filtration, precipitated the *datiscine* in the way already described. I could not, however, observe that the crystals of the *datiscine*, when gelatine had been employed in its preparation, were in the least degree dissimilar from the *datiscine* obtained in the usual way.

Properties of Datiscine.—*Datiscine*, when quite pure, is perfectly colourless; but, unless great attention is paid to its purification, it

* Ann. Ch. Phys. [3], iii. 277.

usually has more or less of a yellow colour, varying from pale to deep yellow, according to circumstances. It is very soluble in alcohol, even in the cold, boiling alcohol dissolving almost any amount of it.

By slow spontaneous evaporation, its alcoholic solutions yield small silky needles arranged in groups. Cold water does not dissolve much of it, but it is tolerably soluble in boiling water, the hot solutions on cooling depositing it in shining scales. Ether does not dissolve much datiscine; but an ethereal solution, when allowed to evaporate as slowly as possible, yielded it in larger crystals than I could have obtained in any other way. When water is added to an alcoholic solution of datiscine, no precipitate is immediately formed, unless the solution is greatly concentrated; but on standing for some time, the datiscine separates in a very pure state, consisting of fine crystals having a pale yellow colour. The datiscine prepared by this process was found to contain but a minute trace of ash. When datiscine is heated to about 180° C., it melts, and if the heat is still further increased, it burns, evolving an odour of caramel, and leaves a voluminous charcoal. If datiscine be heated in a close vessel while a stream of dry air is slowly passed over it, a small quantity of a crystalline substance sublimes. Datiscine and its solutions have a very bitter taste; and though it does not produce any change upon test paper, I think there is reason to regard it as a feebly acid body. It dissolves in solutions of the fixed alkalies and ammonia, as well as in lime and baryta water. Their solutions have a deep yellow colour, which they lose on the addition of an acid, when the datiscine is precipitated, even acetic acid precipitating datiscine. When its alkaline solutions are not too concentrated, and are neutralized while hot, the datiscine on cooling is deposited in small crystals. The aqueous solution of datiscine is precipitated by neutral and basic acetates of lead, or chloride of tin. These precipitates have a bright yellow colour.

Salts of copper produce greenish precipitates; those of peroxide of iron deep brownish-green precipitates. The datiscine employed in these experiments had been purified with gelatine.

The lead salts form such gelatinous precipitates, that they could not be washed, and therefore I was unable to employ them in determining the equivalent of datiscine.

Action of dilute Sulphuric Acid on Datiscine.—When an aqueous solution of datiscine is treated with a small quantity of sulphuric acid, the clear liquid, after being boiled for a few minutes, becomes turbid, and deposits a crystalline substance. This is collected on a filter, and the clear liquid which passes through, after it has been made strongly alkaline by the addition of potash, and after being heated to 212° , throws down suboxide of copper. When the excess of sulphuric acid is removed from

another portion of the solution, by neutralizing with carbonate of lead or baryta, it acquires a sweet taste; and when evaporated to the consistence of a syrup, on standing for some time, it formed a semi-crystalline mass, closely resembling honey. This experiment showed, therefore, that datiscine, like salicine and similar bodies, belongs to the class of glucosides, and is a copulated compound of sugar and another substance which I shall call *datiscetine*.

Datiscetine.—*Datiscetine* in its general appearance and properties closely resembles *datiscine*. On a closer examination, however, these two substances are found to differ essentially, both in composition and properties. *Datiscine*, when prepared by boiling a solution of pure *datiscine* with dilute sulphuric acid, precipitates in the state of fine needles, which are nearly colourless. It is easily soluble in alcohol, a hot alcoholic solution, on cooling, depositing the greater portion of it in crystalline groups. It is almost insoluble in water, and consequently *datiscetine* is abundantly precipitated from its alcoholic solutions by the addition of water. It dissolves in ether to almost any extent, and is deposited, on the evaporation of that liquid, in needles.

These properties of *datiscetine* enable us to obtain it in a tolerably pure state, when even very impure *datiscine* is employed in its preparation. The mother-liquors out of which *datiscine* has been crystallized, and which retain a large amount of impurities, can be used in the following way for the preparation of *datiscetine*. These liquors are first treated with basic acetate of lead, the precipitate is collected on a filter and washed, and then, having been distributed through water, is decomposed by sulphuretted hydrogen. The solution which has filtered from the precipitated sulphide of lead, is then concentrated, and boiled with dilute sulphuric acid. The *datiscetine* produced in this way can be easily separated from the resinous matter, as the latter is precipitated before the formation of the *datiscetine* by the acid, and adheres to the bottom of the flask. By dissolving the *datiscetine* thus obtained in alcohol, and precipitating it by the addition of water, it is rendered tolerably pure.

Properties of Datiscetine.—*Datiscetine* has no taste. When heated it melts like *datiscine*, but the heat required is much higher than is necessary for that body. It crystallizes again on cooling. By operating very cautiously, a portion of the *datiscetine* may be sublimed in crystals. This sublimate, however, appears to be altered *datiscetine*, for, when recrystallized out of ether, it has a sweet taste. *Datiscetine* on burning does not emit the smell of caramel.

Datiscetine, like *datiscine*, dissolves in alkaline solutions, and is reprecipitated by the addition of an acid. When an alcoholic solution of acetate of lead is added to one of *datiscetine*, also dissolved in alcohol, a finely coloured deep yellow precipitate is

obtained, which can be easily washed both by alcohol and water.

This precipitate gave, by analysis, results agreeing with the formula $C_{30}H_8O_{10} + 2PbO$.

| Required. | | | Found. | | |
|-----------|---------|--------|--------|-------|-------|
| C_{30} | = 180.0 | 36.63 | 36.11 | — | 36.09 |
| H_8 | = 8.0 | 1.63 | 1.69 | — | 1.61 |
| O_{10} | = 80.0 | 16.28 | — | — | — |
| $2PbO$ | = 223.4 | 45.46 | 45.22 | 45.13 | 45.73 |
| 491.4 | | 100.00 | | | |

Analysis of Datiscetine.—The different preparations were all dried at $100^\circ C$. in a current of dry air, and burned in the gas furnace. I. and II. were crystallized from alcohol; III. and IV. were precipitated from the alcoholic solution by water.

| Required. | | Found. | | | |
|-----------------------|--------|--------|-------|-------|-------|
| | | I. | II. | III. | IV. |
| C ₃₀ = 180 | 62.94 | 62.89 | 62.90 | 62.88 | 63.03 |
| H ₁₀ = 10 | 3.49 | 3.58 | 3.70 | 3.61 | 3.76 |
| O ₁₂ = 96 | 33.57 | — | — | — | — |
| 286 | 100.00 | | | | |

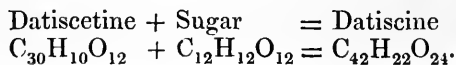
Analysis of Datiscine dried in a Liebig's drying tube.—A. Datiscine crystallized out of alcohol. B. Datiscine crystallized out of alcohol from another preparation. C. Datiscine prepared with gelatine and out of alcohol. D. Datiscine separated from its alcoholic solution by the addition of water. E. Datiscine precipitated from its potash solution by the addition of acetic acid.

The substance analysed in A. contained 0.3 to 0.4 per cent. of ash; that in B. 0.2 to 0.25 per cent.; and that in C. 0.12 per cent. No allowance, however, was made for these amounts of ash in calculating the following numbers.

The datiscine used for the analyses D. and E. did not contain any appreciable quantity of ash.

| | A. | | B. | | C. | D. | | E. |
|---|-------|-------|-------|-------|-------|-------|-------|-------|
| C | 54.79 | 54.38 | 54.79 | 54.73 | 54.97 | 54.11 | 54.48 | 54.27 |
| H | 5.08 | 5.19 | 5.25 | 5.29 | 5.16 | 5.41 | 5.19 | 5.12 |
| O | — | — | — | — | — | — | — | — |

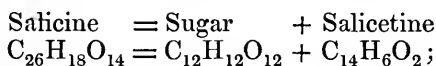
When the decomposition of datiscine into datiscetine and sugar is taken into consideration, it seems probable that the formula for datiscine is



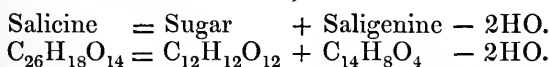
That formula requires

$$\begin{array}{rcl} \text{C}_{42} & = & 252 \qquad 54\cdot08 \\ \text{H}_{22} & = & 22 \qquad 4\cdot72 \\ \text{O}_{24} & = & 192 \qquad 41\cdot20 \end{array}$$

If the formula $\text{C}_{42}\text{H}_{22}\text{O}_{24}$ be correct, the decomposition of datiscine would be analogous to salicine, which, when treated with dilute acid, gives



whilst when treated with emulsine,



The above formula for datiscine is confirmed by the following determinations of sugar formed by treating a weighed quantity of datiscine with dilute sulphuric acid. The quantity of sugar produced was estimated by Fehling's method with a standard solution of sulphate of copper. Four determinations made in this way gave, for 100 parts of dry datiscine, 41·6, 39·5, 39·3, and 37·8 parts of sugar. The calculation for the formula $\text{C}_{42}\text{H}_{22}\text{O}_{24}$ requires 38·6 per cent. of sugar.

An attempt was made to confirm these determinations by the direct estimation of the datiscetine formed during the decomposition of a given weight of datiscine by dilute sulphuric acid. The numbers obtained, however, during different experiments did not correspond with each other, and were all much lower than theory required. This, however, is not to be wondered at, as the datiscetine, though very difficultly soluble, is by no means absolutely insoluble in water. Dilute hydrochloric acid was found, like sulphuric acid, to decompose the datiscine into sugar and datiscetine, and even on boiling an aqueous solution of pure datiscine for some hours, traces of sugar could be detected; thus showing that a small portion of the datiscine had been decomposed. It has been shown by previous experiments, and analysis No. 8, that datiscine may be dissolved in cold solutions of potash without decomposition. When boiled, however, with a concentrated potash-ley for some time, decomposition takes place, and the precipitate, thrown down by the addition of an acid, has all the properties of datiscetine. In this respect, therefore, datiscine agrees with tannin and similar glucosides, which yield the same products when acted upon by acids and alkalies; tannin from nut-galls being equally resolved by acid and alkalies into gallic acid and grape-sugar. A solution of datiscetine, when left for some time in a warm place in contact with yeast, did not ferment; and though emulsine was also tried, no separation of datiscetine was observed.

Action of Nitric Acid on Datiscline and Datiscetine.—When datiscetine is treated in the cold with nitric acid of ordinary strength, a violent reaction takes place, brown vapours are disengaged, and a resinous substance produced. The heat evolved by the reaction is sufficient to continue it till all the resinous matter is dissolved and a dark red liquid produced, which after boiling becomes yellow, and when cautiously evaporated, deposits on cooling crystals of nitropicric acid. If the reaction is not carried too far, no oxalic acid is formed, and the nitropicric acid obtained is very pure, forming large crystals of a pale yellow colour. The following experiments show that these crystals are really nitropicric acid.

When treated in the cold with a concentrated solution of hypochloride of lime, the very characteristic smell of chloropicrine is instantaneously observed. The addition of a solution of potash to a second portion of the acid threw down crystals of very pure nitropicrate of potash, which, when subjected to analysis, gave 18.04 per cent. of potash, the calculated quantity required for nitropicrate of potash being 17.66 per cent. Datiscline treated in the same way yields nitropicric acid as well as oxalic acid. The formation of nitropicric acid by the action of strong nitric acid on datiscline and datiscetine, renders it highly probable that, by employing dilute nitric acid, less highly oxidized products of decomposition might be obtained. Datiscetine was therefore boiled with dilute nitric acid, *i. e.*, nitric acid with ten parts of water; the crystals of datiscetine soon dissolved, and a yellow liquid was obtained, which, when treated with a solution of perchloride of iron, gave a blood-red colour. When the original solution had cooled, pale yellow crystals were deposited. These crystals were very soluble in hot water, and recrystallized on cooling.

They were likewise very soluble in alcohol and ether, and, when deposited by slow evaporation from their alcoholic solutions, they formed nearly colourless crystals of considerable size, having a fine silky lustre. When treated with hypochlorite of lime, they did not evolve chloropicrine in the cold, but readily produced that compound when gently heated. When they were cautiously heated between two watch-glasses, a portion of the substance sublimed in colourless needles. When this acid was heated with an insufficient quantity of water to dissolve it, it melted and recrystallized on cooling. These properties agree with those of nitrosalicylic acid. In order to confirm this hypothesis, the following salts were prepared.

On saturating a solution of the acid with carbonate of baryta, the baryta salt was obtained in yellow crystals. From their solution ammonia threw down another yellow-coloured baryta salt. A solution of the acid likewise produced a crystallized lead

salt. The ammoniacal salt was obtained in orange-coloured needles by saturating the acid with ammonia and crystallizing *in vacuo*. By double decomposition with the ammoniacal salt I prepared the silver combination, which, like all the others, agreed in its properties with Marchand's description of nitrosalicylic acid salts. When subjected to analysis, 0.1695 grm. of the silver salt gave

0.0630 grm. of silver, equal to 37.17 per cent.,

the quantity of silver in nitrosalicylate of silver being 37.24 per cent. When datiscine was allowed to stand in contact with dilute nitric acid in the cold, it gradually dissolved, and the liquid assumed a yellow colour. The solution, when left to evaporate *in vacuo*, was found to contain a mixture of oxalic and nitropicric acids.

Action of Potash on Datiscine and Datiscetine.—It was stated in a previous part of this paper that datiscine and datiscetine dissolve in solutions of caustic alkalies without decomposition, and that datiscine, when boiled for some time, is decomposed with formation of datiscetine. It only remained therefore to try the action of fused hydrate of potash. Datiscetine, when added in small successive portions to fused hydrate of potash, assumed a deep orange colour, and then dissolved with evolution of hydrogen gas. When the disengagement of hydrogen ceased, the mass was dissolved in water and supersaturated with hydrochloric acid. A partly crystalline resinous substance separated, which, by sublimation, yielded perfectly colourless long crystals, closely resembling benzoic acid. Their solution in water assumed, on the addition of perchloride of iron, that deep violet tint which disappears on the addition of hydrochloric acid, and is characteristic of salicylic acid.

Action of Chromic Acid.—Datiscetine was likewise distilled with bichromate of potash and sulphuric acid; the liquid which came over did not contain oily drops, but had the smell of salicylous acid, and formed with persalts of iron a purple-coloured solution.

A trace of salicylous acid appeared therefore to have been produced.

It follows therefore, I think, from the experiment already detailed, that datiscine, like salicine, phloridzine, &c., is a glucoside, and that it approaches nearer to salicine than any other glucoside, with the exception of populine, yet known. In fact I am not aware of any glucoside, with the exception of salicine and populine, which, when treated with nitric acid, yields nitrosalicylic or even nitropicric acid. Phloridzine and phloretine, for instance, when treated with nitric acid, are stated by different experimenters to yield only oxalic acid. I repeated the experiment with phloretine, and obtained much oxalic acid, while the residual liquor yielded not a trace of chloropicrine when treated

with hypochlorite of lime, and consequently contained no nitro-picric acid. Quercitrine, when likewise treated with nitric acid, was also found to yield, as Rigaud states, only oxalic acid. I had no opportunity of trying esculetine, but it is stated by those who have investigated it to yield only oxalic acid.

I will conclude this account of datiscine by proposing the following practical application. As is well known, the colouring matter of madder when boiled with dilute sulphuric acid is changed into sugar and garancine, a new dye-stuff, which for many purposes is found superior to that originally present in the madder.

Within the last twelve months, Mr. Lieshing, by treating the colouring matters in weld and quercitron bark with dilute sulphuric acid, has resolved them into new colouring matters, which are but slightly soluble in water, and are found nearly three times more powerful as dye-stuffs than the original colouring matters from which they had been produced. As datiscine, when boiled with dilute sulphuric acid, undergoes a perfectly similar transformation, being resolved into sugar and datiscetine, which has a much higher colouring power than the datiscine which has produced it, I have not the least doubt that silk-dyers, who may hereafter employ solutions of *Datisca cannabina*, will find it highly advantageous to convert their datiscine into datiscetine by boiling it with dilute sulphuric acid; as the process is an extremely simple one, and as the datiscetine, from its sparing solubility in water, can be very readily obtained in a state of comparative purity.

PTYCHOTIS AJOWAN.

The *Ptychotis Ajowan* is an umbelliferous plant, well known in India for its aromatic and carminative properties. Its seeds, which very much resemble in appearance those of the caraway, only being much smaller, have a very agreeable odour, resembling oil of thyme.

On distilling these seeds repeatedly with water, the essential oil is very easily obtained, amounting to between five and six per cent. of the weight of the seeds. This oil has a light brown colour, and possesses an agreeable aromatic odour. Its specific gravity is 0.896 at 12° C.; and upon leaving the oil for some time in an open dish to spontaneous evaporation, the temperature at the time being comparatively low, large beautiful crystals were deposited, which on examination were found to be identical with the stearopten brought from India by the late Dr. Stocks, and described by me in a short notice published in the number of the "Pharmaceutical Journal" for December 1854. When the crude oil is submitted to distillation, it begins to boil at 160° C., the thermometer rising rapidly to 174° C. The thermometer then rises to 220° C., and the oil which comes over at this temperature

crystallizes on cooling. The residue, which does not immediately crystallize, on remaining at rest for some time, solidifies into a crystalline mass, the crystals having precisely the same form as those obtained by spontaneous evaporation, and amounting, in weight, to from one-third to one-fourth of the crude oil. As it seemed probable from these experiments, therefore, that *Ptychotis* oil, like many other essential oils, is a mixture of a liquid hydrocarbon and of a less volatile oxygenated stearopten, I proceeded to separate these compounds.

The Hydrocarbon.—The more volatile portion of the oil was redistilled, that part of it which boiled at 176° C. being separately collected. After having been dried with chloride of calcium, it was distilled over caustic potash. It was then repeatedly treated with sodium, and again cautiously rectified. The hydrocarbon thus obtained was perfectly colourless, refracted light strongly, and had a pungent, aromatic odour, quite dissimilar, however, from that of oil of thyme. Its boiling-point was found to be 172° C., a thermometer being placed in the vapour, and its specific gravity 0.854 at 12° C. Analysis shows that it is isomeric with oil of turpentine.

| Required. | | Found. | |
|---------------|-------|--------|-------|
| | | I. | II. |
| $C_{10} = 60$ | 88.23 | 88.31 | 88.15 |
| $H_8 = 8$ | 11.77 | 11.59 | 11.49 |
| 68 100.00 | | | |

When the oil was treated with hydrochloric acid, no crystalline compound was obtained, but a brown mobile liquid, having an agreeable smell similar to the oil itself.

The Stearopten.—I have already mentioned that the portion remaining in the retort from the distillation of the crude oil solidified on cooling into a crystalline mass. When cautiously rectified it began to boil at 218° C., the thermometer, towards the latter part of the distillation, rising to 225° C., and even higher. The greater portion, however, came over at about 222° C. The first portion which came over was quite colourless, and had a mild aromatic smell, but the subsequent portions had a more pungent odour, and a yellowish colour. The more volatile, and by far the larger portion of the distillate, crystallized on cooling, especially when agitated, the crystals assuming a rhombohedral form. When it was kept quite quiet, however, it remained liquid for several days, but on being plunged into a freezing mixture it immediately solidified. The less volatile and more coloured portion of the distillate could not be made to crystallize, even when kept in a mixture of snow and salt. The form of the crystals, obtained by the solidification of the distilled stearopten, appeared at first

sight to differ from that of the stearopten from India given me by Dr. Stocks; but, upon these crystals being dissolved in the hydrocarbon of the oil, they were obtained in forms precisely similar to those of the Indian stearopten. This was also the case when either the crude or the distilled crystals were deposited from their solutions in alcohol or ether.

The following are the results of the analyses of the stearopten obtained from different sources.

A. Stearopten from India.* B. Stearopten obtained by the spontaneous evaporation of the oil. C. Distilled stearopten recrystallized from the oil.

| Required. | | Found. | | | | | | |
|----------------------|-------|--------|-------|-------|-------|-------|-------|--|
| | | A. | | | B. | C. | | |
| C ₁₀ = 60 | 80.00 | 79.53 | 79.38 | 79.34 | 79.50 | 80.36 | 80.33 | |
| H ₇ = 7 | 9.33 | 9.43 | 9.19 | 9.19 | 9.06 | 9.09 | 9.38 | |
| O = 8 | 10.67 | — | — | — | — | | | |
| <hr/> | | | | | | | | |
| 75 | | 100.00 | | | | | | |

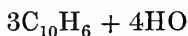
D. Distilled stearopten not recrystallized out of the oil. E. The same crystals recrystallized out of ether and pressed between folds of blotting-paper. F. The last (now crystallizable) part of the distillation.

| D. | | E. | | F. | |
|-----------|-------|-------|-------|-------|-------|
| C = 78.58 | 78.26 | 78.84 | 78.90 | 76.71 | 76.92 |
| H = 9.09 | 9.06 | 9.09 | 9.20 | 9.48 | 9.25 |

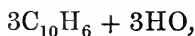
It will be seen, by the above analyses, that, during distillation, the stearopten undergoes partial decomposition, the amount of carbon being thus decreased.

The analyses D. and E. were evidently made with an impure substance, but the analysis F. agrees in a surprising manner with the numbers calculated from the formula C₁₅H₁₁O₂, which requires C 76.92 per cent. and 9.40 H.

I do not, however, wish it to be supposed that the formula given above, or the double of it, viz., C₃₀H₂₂O₄, is the true formula for that substance; nevertheless I may observe that it bears a very simple relation to the formula of the stearopten itself. The one may be regarded as



and the other



that is, as two different hydrates of the same hypothetical hydro-

* In the December Number of the "Pharmaceutical Journal" for 1854, I published an analysis of the stearopten made from a small portion of the substance given me by the late Dr. Stocks. This I have subsequently found to be inaccurate, and the analyses given above are substituted in its stead.

carbon $C_{10}H_6$, or $C_{20}H_{12}$, which perhaps might have been obtained by distilling the stearopten with anhydrous phosphoric acid.

All experiments made with a view of determining the basic or acid properties of the stearopten, gave negative results. When an alcoholic solution of the crystals was mixed with one of acetate of lead, no precipitate was formed, and the same was the case with nitrate and ammonio-nitrate of silver. The crystals of the stearopten dissolve when gently warmed in oil of vitriol, heat being evolved, and a purple colour produced. On standing, the whole solidified, and the mass thus obtained was very soluble in water, yielding a colourless solution, with drops of a red oily liquid floating in it, produced probably by the action of the sulphuric acid on some of the hydrocarbon adhering to the stearopten. When dissolved in a small quantity of hot water, the copulated acid was deposited, on the cooling of the solution, in fine, colourless, scaly crystals. I regret that the small quantity of the substance at my disposal prevented me from determining the equivalent of the stearopten by means of the acid or one of its salts. I obtained both the baryta and the lead salt in a crystallized state by neutralizing the solutions of the acid with the carbonates of those bases. Their analysis, however, gave irregular results, as, owing to the smallness of their quantity, I could not prepare them in a state of perfect purity. In the former notice of the stearopten, already mentioned, it was stated that by long continued digestion with concentrated nitric acid, the stearopten was dissolved, and a colourless crystalline acid produced. This acid is neither oxalic acid, nor, apparently, any of the nitrogenated acids. At least, when warmed with hypochlorite of lime, it gives off no chloropicroine. I suspect, therefore, that it will be found to be a new acid, the examination of which I hope ere long to lay before the Society. From the physical properties and the elementary composition of the stearopten of the *Ptychotis Ajowan*, it struck me that it was very similar to, if not identical with, the solid portion of oil of thyme, described by Lallemand in his recent papers on that substance.* This idea induced me to distil the stearopten dissolved in oil of vitriol with an excess of peroxide of manganese. As anticipated, besides formic acid, there came over yellow drops which solidified on cooling, forming large crystals, having a peculiar odour, somewhat resembling iodine or kinone, and agreeing in every respect with the substance described by Lallemand as thymol.

Before Lallemand has published his experiments in detail, which are now only known from the two notes in the "Comptes Rendus," I do not think it possible to decide with perfect certainty whether thymol and the stearopten of the *Ptychotis* are really identical substances, and even then, perhaps, it will be

* Compt. Rend. de l'Acad. xxvii., 498, and xxxviii., 1022.

found necessary to make more complete experiments with the stearopten of the *Ptychotis*. The hypothesis of their identity, however, appears to me highly probable from the great similarity existing in the most important properties of those substances. I may add, that I agree with Gerhard† in considering the crystallizable substance obtained by Arppe‡ from the essential oil of the Horse-mint (*Monarda punctata*, *huile de monarde*), to be identical with Lallemand's thymol and Doveri's§ less volatile portion of the oil of thyme.

All these substances gave nearly the same numerical results when subjected to analysis.

Doveri observed two boiling-points, one between 175° and 180° C., and the other between 230° and 235° C.

Lallemand found the boiling-point of his thymène to be 165° C., and obtained a liquid hydrochloric acid compound.

Arppe's crystallizable substance from the horse-mint oil was found to melt at 48° C., to solidify at 38° C., and to boil at 224° C.

The crystals were rhombohedral, having one angle of 97° 30' and another of 82° 30'.

The *Ptychotis* oil, according to my experiments, contains a hydrocarbon boiling at 172°, and forming a liquid hydrochloric acid compound, and a crystallizable substance melting at 44° C., and boiling at about 222° C. Two properties, however, I observed different from those given by Lallemand, viz., that the stearopten of the *Ptychotis* is precipitated (in a liquid state) from its alcoholic solutions by water, and that potash does not dissolve it, but merely causes it to assume the liquid state.

From the results of these experiments, therefore, I think we may confidently infer that the stearopten of the *Ptychotis* oil, and the crystallizable oxygenated portion of oil of thyme, examined by Lallemand, if not identical, as I apprehend they are, are certainly extremely similar bodies.

GUM OF THE GARDENIA LUCIDA, Roxb. (*the Decamalee Gum of Scinde*).

The specimen of this gum on which I operated was evidently very old. It formed a hard, dry mass, of a dark brown colour, with numerous patches of greenish-yellow matter disseminated through it. It had but a faint odour, unless freshly fractured or gently heated, when it smelt like the urine of the cat. A comparatively recent specimen of this gum, which I saw in the hands of the late Dr. Stocks, had nearly the consistence of candied

* *Traité de Chimie Organique*, iii, 610.

† *Ann. Ch. Pharm.* lviii, 41; *Chem. Gaz.*, December 1846.

‡ *Ann. Ch. Phys.* [3] xx, 174.

honey, and an exceedingly offensive odour. Dr. Stocks informed me that the recent gum was employed as a dressing for wounds, as it kept off the flies.

The resin was digested in strong spirits of wine till a saturated solution was obtained. This, on cooling, immediately deposited some yellow amorphous flocks. These were separated by filtration, and the clear liquid slowly evaporated *in vacuo*. On standing a few days, it deposited slender golden-yellow crystals, about half an inch in length. The crystals had considerable lustre, and were very brittle. To this crystalline substance I propose giving the provisional name of *Gardenine*.

Gardenine is nearly insoluble both in cold and hot water. It dissolves pretty readily in alcohol, but much less easily in ether, yielding bright yellow solutions, out of which it crystallizes on cooling. Alkalies, such as ammonia, do not appear to increase its solubility. It is slightly soluble in hot hydrochloric acid. Strong oil of vitriol dissolves gardenine in the cold with the production of a beautiful dark red colour. On adding water to this solution, the gardenine is precipitated apparently unchanged. Its alcoholic solutions give no precipitates with ammonio-nitrate of silver, or with basic acetate of lead. When gardenine is digested with concentrated nitric acid, it is rapidly decomposed, nitropicric acid, but apparently no oxalic acid, being produced.

Unfortunately, from the very small quantity of resin at my disposal, I was unable to prepare a sufficient amount of the gardenine, either to subject it to analysis, or to examine it more particularly. Dr. Royle has, however, already commissioned a large quantity of the resin from India, which I trust will ere long enable me to complete its examination.

Gardenine appears to belong to the tolerably numerous class of indifferent crystallizable resins, of which it is certainly one of the most beautiful.

NOTES ON *Datisca cannabina*, *Ajowan*, AND *Decamalee Gum*,
received from DR. ROYLE, MARCH 12, 1856.

Ikl-beer, the stems and roots of *Datisca cannabina*.—" *Datisca* is found both in the Old and New World, existing in the latter in Pennsylvania. *D. cannabina*, so named from its great resemblance to the Hemp-plant, extends from the south of Europe and Asia Minor through Iberia to the valleys of the Himalaya. I have obtained it from Cashmere and Kunawm, and found it at the foot of the Choor and Kedarkanta mountains. It spreads also to Nepal; *D. nepalensis*, Don, being the same species."—Royle, *Himal. Bot.* p. 340.

The *Ikl-beer* is much esteemed in the Punjab for dyeing silk of a yellow colour. It is probable that some of the silk scarves of a

lemon-yellow colour, which were much admired by artists for the delicacy of their colour, had been dyed by this substance, as it is there esteemed for dyeing silk of this colour.

Ajwain.—"The remaining Umbelliferae, which are known in India, are those found only in a cultivated state; but this from so remote a period as to have become perfectly naturalized, and known to the natives, as well as to have names given to them in the languages of different parts of the country; some also have not as yet been found in other parts of the world;"—"as *Ptychotis Ajowan*, known everywhere by the name *Ajwain*, slightly varied in different districts."—"In addition to these, *Ptychotis sylvestris*, nob., called *arub ajwain*, is used as a carminative by the natives."—Royle, *Himalaya Bot.* p. 229.

"Dr. Roxburgh, in describing *Ligusticum Ajowan*, states, he cannot conceive that this famous Indian plant, aromatic in smell, pungent in taste, used both by natives and Europeans for culinary and medicinal purposes, can be unknown to European botanists. To *Ajwain* Persian authors assign *nankhwah* as the Arabic name. This is the Nankhwah of Avicenna, written *nanachua* and *nanachue* in the marginal translation of Ammi, in the Latin edition of his works; which names are quoted under Ammi by Mathioli, in his Commentaries on Dioscorides. But in Persian works on *Materia Medica*, Aammi is also given as the Greek synonym of *nankhwah*, that is, of *Ajwain*, which Dr. Roxburgh justly supposed could not be unknown to Europeans. This plant has been referred by M. De Candolle to the genus *Ptychotis*, which brings it near *P. copticum*, called at one time *Ammi copticum*: the Ammi itself is called *Cuminum Æthiopicum* and *regium*; the latter name is translated by Kumoon Mullookce, and is given as a synonym of *nankhwah* in Persian authors."—*L. c.* p. 230. It is probable therefore that this Indian species of *Ptychotis* has long been employed as the Aammi of the Greeks.

Decamalee.—"This is the gum of the *Gardenia lucida*. It exudes in amber-coloured transparent drops, at the ends of the young shoots, and from thence is collected. It is most useful in preventing vermin from breeding in wounds. It is brought to Bombay from the interior."—*Bombay List of Articles for Exhibition of 1851*, p. 30.

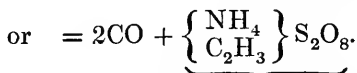
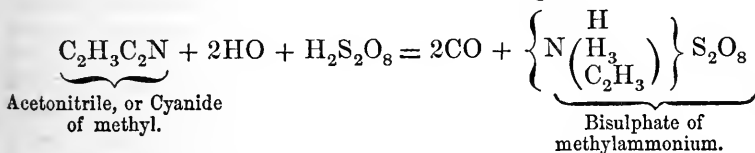
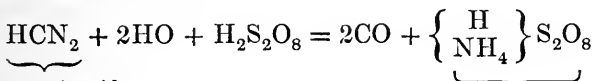
Researches on the Action of Sulphuric Acid upon the Amides and Nitriles, together with remarks upon the Conjugate Sulpho-acids.

By George B. Buckton, Esq., F.L.S., F.C.S., and A. W. Hofmann, L.L.D., Ph.D., F.R.S., &c.

Read before the Royal Society June 12, 1856.

EVER since the experiments of Dumas, Malaguti, and Leblanc on the one hand, and those of Kolbe and Frankland on the other, have established the identity of the hydrocyanic ethers with the nitriles, it has been a favourite problem with chemists to reproduce the alcohols from these bodies, the solution of which would afford a passage from an acid $C_{2n}H_{2n}O_4$, to an alcohol $C_{2n-2}H_{2n}O_2$.

We have been likewise engaged with this question. The deportment of hydrocyanic acid (formonitrile) under the influence of concentrated sulphuric acid, which, as is well known, gives rise to an evolution of carbonic oxide, suggested an examination of the other nitriles in a similar direction. There appeared to be a chance of producing in this manner from a nitrile, the sulpho-vinic acid of an alcohol containing two equivalents of carbon less than the nitrile. Acetonitrile, for instance, might have been thus converted either into sulphate of methylammonium or into sulphomethylate of ammonium.



Experiment has not corroborated either of these anticipations. This reaction gives rise to the formation of a remarkable conjugate sulpho-acid, which may be considered as the type of a most extensive class of analogous compounds, some isolated terms of which have been met with already in previous investigations.

Before, however, detailing the conditions under which these

new bodies are formed, it may not be unacceptable to make a few statements regarding the most efficient method of procuring the nitrile of the methyl-series in quantity and in a state of purity.

PREPARATION OF ACETONITRILE.

The preparation of cyanide of methyl (acetonitrile), by decomposing sulphomethylate of potassium with cyanide of potassium, is unsatisfactory, both as to quantity and quality of the product obtained. The presence of a minute amount of moisture in the materials employed gives rise to a number of secondary products, the chief of which are cyanide and carbonate of ammonium, and a gas possessing a highly offensive odour, which imparts to the distillate a smell not at all due to the nitrile itself. By far the most advantageous method of preparing acetonitrile consists in acting upon acetamide with anhydrous phosphoric acid, as proposed by M. Dumas.

Acetic ether is not immediately soluble in a moderate quantity of aqueous ammonia; but after five or six hours' contact, the layers at first formed disappear, and the liquid becomes homogeneous.

If distillation be now at once commenced, scarcely a trace of acetamide will be obtained. The change, on the other hand, is complete if the mixture be exposed for some hours to a temperature of 120° or 130° C.

We have employed in this operation a wrought-iron cylinder, similar to that used by Dr. Frankland in his researches, which had been constructed for us by Mr. James Nasmyth, who never fails most kindly and liberally to lend the extraordinary resources of his celebrated establishment for scientific purposes. Equal volumes of acetic ether and concentrated ammonia were introduced into the boiler, the brass valve of which was protected from corrosion by a steel screw and leaden washer. After six hours' digestion, the acetamide was separated by distillation with the thermometer from the alcohol formed, that part only being reserved as anhydrous which had passed over above 200° . When acetamide is intimately mixed with about an equal volume of anhydrous phosphoric acid in a retort, a powerful action commences immediately, and the nitrile passes over colourless, but contaminated with acetic and hydrocyanic acids. Towards the end of the operation, it is necessary to use a strong heat to drive off the last portions. The distillate is now agitated with just sufficient aqueous potash to neutralize the acids, when the nitrile floats on the surface, and may be removed for rectification over a fresh quantity of phosphoric acid, to render it perfectly anhydrous. Pure acetonitrile possesses an ethereal odour, faintly recalling that of cyanogen; its aromatic taste is pungent, but not disagreeable.

We observed the boiling-point 77° — 78° , which coincides with that observed by Dumas. It does not appear to have been previously noticed, that acetonitrile burns with a luminous flame, the edges of which are beautifully tinged with peach-blossom colour. The flame and odour of acetonitrile unmistakably bespeak the cyanic relations of this compound.

ACTION OF SULPHURIC ACID ON ACETONITRILE.

This body, when mixed with its own volume of fuming sulphuric acid, gives rise to a very energetic reaction, a considerable amount of heat being evolved, which causes much of the nitrile to volatilize and thus escape decomposition. In order to avoid this, the operation is best conducted in a retort surrounded with cold water, when a perfect mixture can be effected, scarcely a change of colour becoming perceptible. On application of heat, the mixture intumesces powerfully with copious evolution of a gas which, on examination over mercury, proves to be carbonic acid, without a trace of carbonic oxide; at the same time strong acetic acid passes into the receiver. If the temperature be kept up by the gas-flame until the effervescence almost entirely ceases, the mass when cold forms a brown, tough, and transparent solid, readily soluble in water and in alcohol. The aqueous solution, boiled with an excess of carbonate of barium, is then passed through a hot-water filter, when a magnificent salt is deposited, in the form of brilliant colourless rectangular plates which, when gathered in mass, exhibit a nacreous lustre. This salt is remarkably stable. It loses no weight at 100° C., but gives off water of crystallization somewhat below 150° . At a temperature of 220° the substance still remains unaltered, but when heated beyond this point, it begins to turn yellow, and disengages water, sulphurous acid and carbonic oxide, whilst sulphur sublimes. When strongly heated, it becomes incandescent, leaving a residue of sulphate and sulphite of barium. The new salt may be crystallized unchanged from hydrochloric acid, and may be boiled for hours with concentrated nitric acid, without formation of sulphate of barium. It is quite insoluble in alcohol.

ACTION OF SULPHURIC ACID UPON ACETAMIDE.

As acetamide differs from acetonitrile only in containing two additional equivalents of water, this compound, when heated with fuming sulphuric acid, undergoes a perfectly analogous transformation.

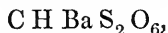
From the comparative facility of its preparation, acetamide offers peculiar advantages for procuring the new substance in large quantity. The chief difficulty which presents itself consists in

operating with the right proportions of acid and amide. Distillation of equal volumes of dry acetamide and ordinary Nordhausen acid, for instance, gives scarcely a trace of anything but acetic acid and sulphate of ammonia. The most efficient proportions we found to be two volumes of amide to three volumes of acid. The distillation should be pushed very far, in fact until the product of distillation is accompanied by sulphurous acid. The solution of the solid residue may at once be saturated with carbonate of barium; it will be found, however, more economical to treat the liquid with finely-powdered Carrara marble until the free acid is neutralized, and to reserve the pure carbonate of barium, which is so difficult to wash thoroughly, merely for decomposing the sulphate of ammonium towards the end of the process. The liquid must be boiled with excess of the carbonate until a filtered sample ceases to give an insoluble precipitate with chloride of barium. The liquid thus obtained contains now in solution chiefly two ammonium-salts, one of which is scarcely crystallizable, whilst the other forms large and regular rhombic crystals, sometimes an inch in diameter. In addition to these ammonium-salts, a certain quantity of barium- and even calcium-salts are present, which it is necessary to decompose by carbonate of ammonium in excess before an attempt is made to effect a separation of the two salts.

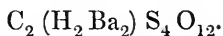
On adding a saturated solution of either chloride or acetate of barium to a moderately strong solution of the crystallized ammonium-salt, the liquid becomes, in the course of a few minutes, nearly solid from the deposition of a mass of crystals of a barium-compound, which may be collected on a filter and well washed with cold water to free it from the chloride of ammonium and excess of the precipitant.

One recrystallization from boiling water furnishes this salt in a state of purity. It in no manner differs from the barium-salt previously described as procured from acetonitrile. The identity is moreover proved by analysis.

From the analytical data we calculate for the anhydrous salt the formula

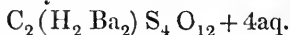


but considerations which we shall develop hereafter, especially the production of similar compounds in analogous series, induce us to double this expression, and to represent the new barium-salt by the formula,



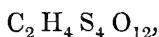
The salt, as already stated, retains water of crystallization at 100°C . In two determinations this water was found to amount to 2 equivalents.

The formula of the crystallized salt is therefore

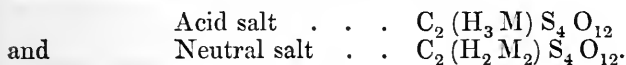


We propose for this substance the name *disulphometholate of barium*, and for the acid the term *disulphometholic acid*, without wishing, however, to express by this term any particular view regarding the actual arrangement of the constituent molecules in the substance.

If the formula above given be correct, disulphometholate of barium is the salt of a bibasic acid, the composition of which would be represented by the expression



furnishing salts of the general formula,



The barium-salt which has been described belongs to the second class.

We have not yet succeeded in preparing any acid salts. Disulphometholate of barium crystallizes unchanged from a hydrochloric acid solution.

Disulphometholic Acid.—To prepare this acid, the barium-salt is precipitated by a small excess of sulphuric acid, which is again removed by means of oxide of lead. Hydrosulphuric acid is then passed through the liquid, which thus becomes strongly acid. It may be concentrated to a syrup without decomposition, and even carefully heated until white fumes appear. On cooling the liquid thus concentrated under the receiver of the air-pump, a crystalline mass of fine radiated needles is produced, exceedingly soluble in water and very deliquescent. They have a pure acid taste, with somewhat the flavour of tartaric acid. The attraction of this acid for water is so great, that we have failed in obtaining it in a solid condition by evaporation over sulphuric acid.

It is not changed by boiling with nitric acid, and chlorine gas passed through the aqueous solution does not liberate sulphuric acid.

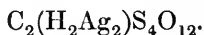
The corresponding salts are readily obtained by digesting the oxides or the carbonates of the various metals with solution of the acid. The barium-salt is immediately precipitated by adding chloride of barium to this solution. The salts are all soluble in water, but insoluble in alcohol.

Disulphometholate of Silver crystallizes either in tufts of flat needles, or in broad tables of considerable size. It is produced when the aqueous solution of the acid is neutralized with carbonate or oxide of silver. We had hoped to obtain crystals of sufficient regularity for measurement of the angles; but although they may be easily produced of sufficient size, the edges are mostly rounded and imperfect.

It bears a temperature of 150° C without decomposition, but

blackens and froths when strongly heated, yielding sulphur, sulphurous acid, and metallic silver. It is insoluble in absolute alcohol, but may be crystallized from spirits of wine.

This salt contains



Disulphometholate of Ammonium.—The formation of this substance has been already described. It is sparingly soluble in cold, but very soluble in hot water; from which it is again deposited in colourless crystals, often an inch in length. They are anhydrous, decrepitate when heated, and bear a temperature of 190° without being changed.

Through the kindness of Mr. Charles Brooke, we are enabled to state that the crystals of this salt belong to the oblique prismatic system, which is in fact nothing more than a hemihedral form of the right prismatic system.

When submitted to analysis, this salt gave numbers corresponding with the formula



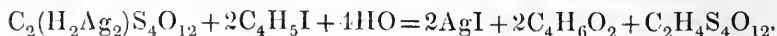
Disulphometholate of Potassium is most readily obtained by adding the crystallized barium-salt by degrees to a boiling solution of carbonate of potassium, avoiding an excess of the former. After filtration, the new substance separates easily from excess of alkali in fine shining needles or brilliant grains, according to the rapid or slow precipitation from its solution. It is not very soluble in cold water, one part requiring fourteen parts of water at 22° C for solution.

Disulphometholate of Zinc.—When metallic zinc is heated with an aqueous solution of the acid, hydrogen gas is liberated, and on concentration, a syrup is formed which crystallizes with great difficulty. Alcohol does not precipitate this salt from its solution.

Disulphometholate of Lead forms small square nacreous plates not unlike those of the barium-compound. It is very soluble in water.

Disulphometholate of Copper is produced by careful precipitation of the barium-salt by sulphate of copper. It yields radiated needles or small prisms of a green colour. They are insoluble in absolute alcohol, but soluble in spirits of wine.

We have not succeeded in preparing the ethers of this acid. We anticipated that they would be formed by bringing together iodide of ethyl and disulphometholate of silver. A strong solution of the silver-salt reacts at once on the iodide without application of heat. Iodide of silver is precipitated; but the ether which is formed splits immediately into disulphometholic acid and alcohol, according to the equation



EXAMINATION OF THE MOTHER-LIQUOR OF DISULPHOMETHOLATE OF AMMONIUM.

Sulphacetate of Ammonium and Sulphacetate of Barium.

It has been already noticed that another salt is present in the mother-liquid obtained during the purification of disulphometholate of ammonium. To procure this substance in a state of purity, the mother-liquid was concentrated, and the crystals of the disulphometholate removed from the thick syrup as completely as possible.

After a moderate addition of cold water, the liquid was mixed with an excess of chloride of barium, and the whole allowed to stand for five or six minutes, when it was filtered, and the filtrate set apart for twenty-four hours. At the expiration of this time, a copious granular precipitate had formed which was well washed with cold water, and then recrystallized from boiling water, in which, when once deposited, it proved to be very little soluble.

This substance differs both in its crystalline form and in its reactions from the disulphometholate. When strongly heated, it turns black and burns away like tinder. The residuary mass, moistened with hydrochloric acid, evolves hydrosulphuric and sulphurous acid, according to the time of ignition.

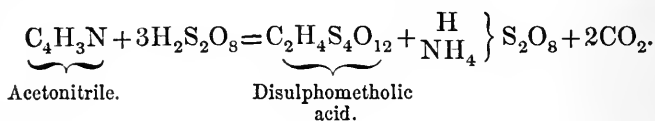
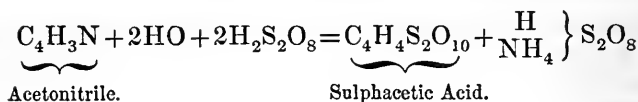
The percentage of barium, obtained in the analysis of this salt, agrees well with the amount required by the formula, $C_4(H_2Ba_2)S_2O_{10}$, of sulphacetate of barium.

The quantity of sulphacetate of ammonium produced, mainly depends upon the degree of heat maintained during the reaction of sulphuric acid upon acetamide or acetonitrile. If the mixture be made gradually and cooled after each addition of acid, the elimination of carbonic acid may be entirely prevented, and the chief product is then sulphacetic acid. On the other hand, if the heat be urged as far as is practicable, disulphometholic acid takes the place of the sulphacetic, carbonic acid being evolved at the same time.

Two phases may therefore be traced in the reaction. In the first, nascent acetic acid simply combines with the elements of two equivalents of anhydrous sulphuric acid. In the second phase, the acetic molecule undergoes a more thorough transformation, splitting, as it does, into carbonic acid and marsh-gas, the latter of which combines with the elements of four equivalents of anhydrous sulphuric acid.

The new acid may also be regarded as sulphacetic acid, which, losing carbonic acid, has assimilated an equal number of equivalents of anhydrous sulphuric acid. ^

The two stages in the action of sulphuric acid on acetonitrile may be represented by the following equations:—



Acetamide containing but two equivalents of water more than acetonitrile, the production of sulphacetic acid and disulphometholic acid from this substance is intelligible by means of the same equations.

The action then of bases and of acids upon acetic acid presents a remarkable analogy. Under the influence of both agents, we may assume, it splits into marsh-gas and carbonic acid; in the first case, it is the carbonic acid which is fixed by the alkali, whilst in the latter the marsh-gas remains in combination with the acid.

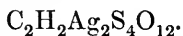
The possibility of assuming the existence of marsh-gas in disulphometholic acid, suggested the idea of endeavouring to combine marsh-gas directly with sulphuric acid. The dry gas obtained by the distillation of acetate of soda with potash-lime was passed into a receiver charged for this purpose with anhydrous sulphuric acid, but we could not detect any combination of the two bodies, either at the ordinary temperature or when the receiver was heated to 100° C. The sulphuric acid, after treatment with water and carbonate of barium, furnished no soluble salt whatever.

Although we have thus been unable to convert marsh-gas into disulphometholic acid, we have found that this acid may be readily transformed into marsh-gas. When heated with hydrate of baryta the salts of the acid yield marsh-gas, together with sulphate and sulphite of barium. A method is thus indicated by which probably all the hydrocarbons, $\text{C}_{n-2}\text{H}_{n-2}$, may be prepared from the corresponding sulpho-acids.*

The simplicity of relation which exists between sulphacetic and disulphometholic acid, left no doubt in our mind regarding the convertibility of the former into the latter. We have established this fact moreover experimentally. Sulphacetic acid, prepared by the action of anhydrous sulphuric acid upon glacial acetic acid, furnished without difficulty disulphometholic acid, when again treated with sulphuric acid. A similar observation had in fact been made already by M. Melsens. This chemist, in his researches upon the sulphacetates, appears in some sort to have anticipated

* We are unable to corroborate M. Aimée's remarks, that marsh-gas is decomposed by sulphuric acid into water, carbon, and sulphurous acid. The acid remains colourless, and the gas after the process exhibits its usual properties unmodified.

the existence of the disulphometholates. He remarks that he once found in the mother-liquor, obtained from the preparation of sulphacetate of silver, a crystalline salt the composition of which he represents by the formula



It is evident that this was nothing but the disulphometholate of silver, but M. Melsens does not appear to have investigated the subject further, or to have connected the appearance of this salt with the evolution of carbonic acid gas, which he likewise found among the secondary products of the action of sulphuric acid upon acetic acid.

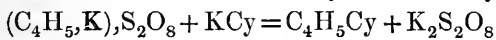
The chemical character of disulphometholic acid is so marked and the reaction which produces it so simple and definite, that there could be no doubt regarding the existence of numerous corresponding terms in homologous and even in analogous series of substances. In fact disulphometholic acid may be considered as the type of a very numerous class of bodies of similar composition, some of which are actually known, while a great many remain to be discovered.

We have ourselves traced the formation of the homologues and analogues of disulphometholic acid in several higher series of bodies, but we have been satisfied in establishing the existence of these substances, without entering into a detailed study of their properties.

ETHYL-SERIES.

Preparation of Propionitrile.

The formation of cyanide of ethyl (propionitrile) by means of cyanide and sulphovinate of potassium, has all the disadvantages above enumerated in the case of cyanide of methyl. A large quantity of an inflammable gas of a highly offensive odour is disengaged, the annoyance of which may be avoided by conducting the gas from the receiver of the liquid into the cylinder of a wire gauze burner, in the air-flame of which it is perfectly consumed. In the preparation of cyanide of ethyl by means of cyanide and sulphovinate of potassium, through the intervention of unavoidable moisture, a variety of different reactions appear to proceed side by side. Together with the formation of cyanide of ethyl,



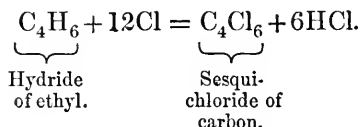
Sulphovinate of
potassium.

Cyanide of
ethyl.

considerable quantities of carbonate of ammonium are produced, whilst an inflammable gas is largely generated, which is nothing but hydride of ethyl. This gas is not absorbed by bromine; it therefore cannot contain any ethylene. It combines with chlorine,

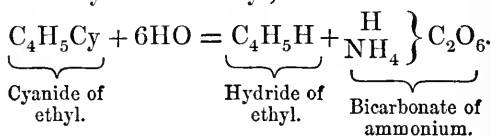
forming a gaseous compound, burning with a green-edged flame. This is probably the substance obtained by Drs. Kolbe and Frankland when treating ethyl with chlorine gas, isomeric with chloride of ethyl, C_4H_5Cl . When in contact with excess of chlorine it yields an oily substance, and a crystalline body having the properties and composition of sesquichloride of carbon.

It is from this fact chiefly that we infer the identity of the inflammable gas generated in the preparation of propionitrile with hydride of ethyl,



The oily liquid observed obviously consisted of the intermediate substitution-terms.

These substances are evidently secondary products of the decomposition of cyanide of ethyl,



Cyanide of ammonium is likewise invariably present, prussic acid being generated by the action of water upon the cyanide of potassium, while alcohol is reproduced to a very considerable extent. Lastly, this process gives rise to a most remarkable body with a most insupportable prussic smell, the formation of which we have traced in a great variety of reactions. We have not completed the study of this compound.

The method finally adopted for obtaining propionitrile in sufficient quantity for us to experiment upon was that recommended by Dr. Williamson, viz., the digestion of cyanide of potassium with iodide of ethyl in four volumes of alcohol as a vehicle. The presence of so much alcohol, from which the cyanide cannot be separated by rectification, on account of the similarity of their boiling-points, is an evil which unfortunately involves a series of tedious processes, namely, conversion of the nitrile into propionate of potassium, by the action of caustic potassa, separation of the alcohol by distillation, preparation of propionic ether, transformation of the latter into propionamide by the action of ammonia under pressure, action of phosphoric acid upon propionamide to form the nitrile, and ultimately dehydration of the nitrile by means of anhydrous phosphoric acid.

In preparing disulphetholic acid we have almost invariably employed propionamide, on account of its easier preparation.

We have, however, established by experiment that propionitrile exhibits with sulphuric acid exactly the same deportment as propionamide. To effect the transformation of the propionamide with success, it is necessary to employ this substance in a perfectly anhydrous condition. Unless this point be properly attended to, sulphuric acid produces principally sulphate of ammonium and propionic acid; for this purpose the amide should be heated in a retort, and that portion only collected which passes over above the temperature of 210° C. Below this point the amide retains sufficient water to prevent perfect crystallization.

On mixing equal volumes of melted amide and fuming sulphuric acid, very considerable heat is disengaged; the temperature must be regularly maintained until carbonic acid ceases to be evolved and propionic acid no longer distils over. Some experiments are necessary in order to fix the quantity of acid required for the conversion of the propionamide, since commercial Nordhausen acid varies considerably in composition. If too much acid be employed, the mixture is often perfectly carbonized, whilst too little acid gives rise to the formation of either sulphopropionic or propionic acid.

If care be taken to regulate the heat so as just to keep up the liberation of carbonic acid, the amount of disulphetholic acid may be considerably increased.

The solid residue in the retort, when cold, is dissolved in water, and treated, as in the case of disulphometholic acid, first with carbonate of barium, and subsequently with carbonate of ammonium. On evaporation the liquid thus obtained furnishes two salts, one of which is quite uncrystallizable, and must be separated from the other by washing with weak spirit. A crystalline substance remains on the filter, which, after two or three crystallizations from hot water, is the pure

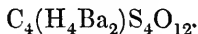
Disulphetholate of Ammonium.—When deposited from an aqueous solution, this salt forms regular cubic crystals or square prisms, perfectly colourless. It is insoluble in alcohol and in ether. In its general behaviour this substance differs but little from the corresponding salt of the methyl-series, the principal feature of difference being a greater solubility and its leaving a carbonaceous residue when strongly heated.

Disulphetholate of Barium crystallizes with regularity in six-sided plates, which generally arrange themselves from centres. It is easily formed by heating a solution of the ammonium-salt with hydrate of baryta until every trace of ammonia is expelled, and then passing a current of carbonic acid through the solution to remove the excess of baryta. It is very soluble in water, and stable at a temperature of 180° , but blackens when strongly heated in close vessels, empyreumatic vapours being at the same time given off. The black residue burns with a sulphur-flame.

Disulphetholate of barium is insoluble in concentrated nitric acid, which does not decompose it. It crystallizes from the dilute acid without apparent change.

After fusion with chlorate of potassium and carbonate of sodium, the filtrate contains sulphates in solution, proving that there is more sulphur present than is required for saturating the barium of the compound. By this method the disulphetholates can be distinguished from the sulphopropionates presently to be described.

On analysis the barium-salt furnished numbers which accord with the formula



A determination of the water renders it probable that the salt contains 2 equivalents of water.

As has been already stated, the disulphethylates may also be prepared from propionitrile. For this purpose three parts of the propionitrile are distilled with two parts of fuming sulphuric acid. As the action is very energetic, the mixing should be effected by degrees in a moderate-sized retort. A barium-salt was prepared the properties of which agreed in every respect with those of the compound prepared from propionamide.

Disulphetholic Acid is obtained by decomposing the lead-salt by hydrosulphuric acid. By concentration it forms a thick syrup, which ultimately solidifies into a crystalline mass. By heat it decomposes with deposition of charcoal and production of white fumes.

Disulphetholate of Silver may be obtained by a process similar to that employed in the case of the disulphometholate. It is crystalline. When dry, it bears a considerable heat without change. The solution blackens on ebullition.

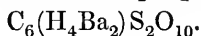
Disulphetholate of Lead is very soluble in water. When evaporated over sulphuric acid, the salt yields fine prisms or minute quadrangular laminae. When hastily evaporated it produces a tough gummy mass.

Sulphopropionic Acid.—As might have been anticipated from the results obtained in the methyl-series, disulphetholic acid is by no means the sole product of the action of sulphuric acid upon propionamide and propionitrile. The formation of this acid is preceded by that of another acid richer in carbon and poorer in sulphur, in one word, by that of sulphopropionic acid. The uncrystallizable ammonium-salt, already mentioned, is in fact the sulphopropionate of ammonium. Absolute alcohol throws it down from its solution as a thick treacly mass, with an appearance very unprepossessing to the analyst. The dilute aqueous solution was therefore boiled with carbonate of barium until entirely decomposed, and the filtered liquid concentrated in a beaker. At a particular point of the evaporation, a quantity of *sulphopropionate of*

barium appeared in small cubic grains, which caused so much "bumping" as to make it necessary to evaporate upon the water-bath.

If the concentration be arrested before the deposition of these grains, and the liquid be set aside for twenty-four hours, it yields a plentiful crop of beautiful silky crystals, arranged in spherical groups.

After another crystallization from hot water, in which the substance is moderately soluble, this salt is sufficiently pure for analysis. It was dried at 170° , and gave on analysis numbers which agree with the formula of sulphopropionate of barium,



PROPYL-SERIES.

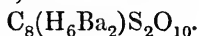
From what has been already said, but few words are necessary on the preparation of disulphopropiolic and sulphobutyric acid. It may, however, be stated, that butyramide boils at 116° , and passes over at that temperature in drops which crystallize beautifully. It has the characteristic sweet taste of the other amides of the series, and, like them, it fumes slightly in the air when gently heated.

Three parts of butyramide produce with two parts of fuming sulphuric acid a horny mass, which, after removal of the sulphuric acid and saturation with ammonia, yields a syrup wholly uncrystallizable. The ammonium-salts were converted into barium-salts, which also possess but feeble powers of crystallization.

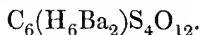
M. Redtenbacher has already pointed out how much the solubility in water of the barium-salts of the acids $\text{C}_{2n}\text{H}_{2n}\text{O}_4$ augments as the value of the coefficient n progressively increases. A similar increase of solubility is observed with the barium-salts of the series of conjugated acids which form the subject of this paper. The contrast between the almost insoluble disulphometholate and the very soluble disulphopropiolate of barium is very marked.

From the extreme solubility of these salts, great difficulty was experienced in separating them completely one from the other. The method adopted was that of partial precipitation by alcohol. To solutions moderately concentrated and cold, sufficient absolute alcohol was added to produce a cloud, permanent when rapidly stirred. On allowing the liquid to stand for an hour, a quantity of a granular substance attached itself to the glass vessel, which, after solution in water and reprecipitation, was dried and decomposed by sulphuric acid.

A barium-determination in the salt led to the formula for sulphobutyrate of barium,



We have not been able to procure the disulphopropiolate of barium in a state of purity. The alcoholic liquid which remains after deposition of the sulphobutyrate contains a considerable quantity of the salt, but so mixed, that we were unable more than proximately to isolate it. By continuing the process of fractional precipitation, and drying, and by analysing the different samples, the quantity of barium present in the successive specimens was found to decrease, the last and lowest number agreeing nearly with the formula of disulphopropiolate of barium,



This salt is not so wholly uncrystallizable as the sulphobutyrate. By slow evaporation it furnishes very minute crystals, which under the microscope show themselves as thin pearly plates. They appear best when slowly thrown down by alcohol from the solution.

BUTYL-SERIES.

Our experiments in this series have been entirely qualitative. We have been satisfied to establish experimentally the analogy of the reactions. These reactions, however, become less and less definite, and, owing to the still greater solubility of the new products, their separation is attended with difficulties almost insurmountable.

The researches detailed on the preceding pages are quite sufficient to establish the general character of the action of sulphuric acid upon the amides and nitriles. Nevertheless, since these experiments exclusively refer to the derivatives of several *homologous* terms of the series of *fatty* acids, it appeared desirable to extend the investigation to a nitrile of the *analogous* group of *aromatic* acids. No substance appeared to be more appropriate for such an examination than benzonitrile, or cyanide of phenyl.

PHENYL-SERIES.

Preparation of Benzonitrile.

M. Fehling originally obtained benzonitrile by subjecting benzoate of ammonium to repeated dry distillations, when the four equivalents of water gradually separated. The process is however objectionable, on account of the necessity of repeatedly returning by hand the sublimed salt to the volatilizing vessel. We hoped to have found a more convenient method, in submitting the same salt to the dehydrating action of chloride of zinc; but on rectifying the distillate, we obtained only one-third of the product in the form of benzonitrile, the remaining portion being

benzole. The safest, but somewhat lengthened, process for procuring benzonitrile, consists in dehydrating benzamide with anhydrous phosphoric acid, the former body having been produced by the action of carbonate of ammonium upon chloride of benzoyl, as recommended by M. Gerhardt.

ACTION OF SULPHURIC ACID UPON BENZONITRILE.

Sulphuric acid and benzonitrile mix with liberation of far less heat than is observable in the cases previously recounted. No gas is disengaged until the temperature is very considerably raised, when a portion of benzoic acid sublimes in the neck of the retort and carbon is deposited, while sulphurous acid is simultaneously disengaged. The action was continued for some time after the appearance of sulphurous acid, for the purpose of decomposing the sulphobenzoic acid which analogy would lead us to expect among the products of the reaction. On cooling, a semi-transparent hard mass of glassy fracture remained in the retort. The usual treatment with carbonate of barium evolved ammonia, showing the presence of a salt of that base.

Sulphobenzoate of Barium.—As the filtrate was very dark-coloured, the barium-salt was again decomposed by sulphuric acid, and then boiled with excess of oxide of lead, filtered and treated by hydrosulphuric acid. The sulphide of lead was found to carry down with it almost the whole of the colouring matter. The acid liquid was then saturated with carbonate of barium, a portion evaporated nearly to dryness and treated with hydrochloric acid, when a salt crystallized out from the mother-liquor, which, after washing with water, was again crystallized until free from hydrochloric acid.

Dried at 200° , it gave a percentage of barium which coincided with that required by the formula $C_{14}(H_5Ba)S_2O_{10}$ of the acid sulphobenzoate of barium analysed by Mitscherlich and Fehling.

It was therefore obvious that the disulphosalt, if present, was the most soluble, and to be found in the filtrate.

The remaining portion of the neutral solution of the barium salt was therefore dissolved in water, and about one-half of the solid matter precipitated by alcohol filtered off and recrystallized, the percentage of barium in which was found to correspond to the neutral sulphobenzoate of barium, $C_{14}(H_4Ba_2)S_2O_{10}$.

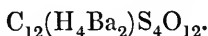
Disulphobenzoate of Barium.—It remained, therefore, to examine the salt last thrown down by alcohol, which, after being purified again by precipitation, gave analytical numbers characterizing the new salt, although still in a state of admixture with sulphobenzoate of barium.

The results of the analysis, leading unequivocally to the

formula $C_{12}(H_4Ba_2)S_4O_{12}$ could leave no doubt regarding the nature of the substance analysed, yet it was desirable, if possible, to prepare the new compound in a state of purity; and the question presented itself, whether it could not be more directly formed from sulphobenzolic acid, $C_{12}H_6S_2O_6$, which is so easily obtained by the action of sulphuric acid upon benzol. Success in its preparation by this means was of considerable interest, since in this case it would become highly probable that all the new bodies hitherto described in this memoir might be prepared, from the analogues of sulphobenzolic acid in their respective groups, by a simple assimilation of the elements of sulphuric acid. The method in question is in reality by far the best adapted for procuring the new acid in a state of purity. Sulphobenzolic acid obtained from the lead- or copper-salt is evaporated on the sand bath until the evolution of white fumes proves that the greater part of the water has been volatilized. It is advisable to heat the solution until a slight brown coloration indicates incipient decomposition. The acid is then introduced into a dry retort, together with an equal volume of strong Nordhausen acid, and the whole maintained at the boiling-point for two hours. The liquid is then reduced by evaporation nearly to the original bulk of the sulphobenzolic acid employed. The new acid in this stage has a very dark colour which cannot be removed by boiling with charcoal. Treatment, however, with an excess of oxide of lead, and decomposition of the filtrate by hydrosulphuric acid, furnishes a liquid which is perfectly colourless.

When this liquid is saturated with carbonate of barium and evaporated, an apparently amorphous mass is produced which, however, under the microscope is distinctly crystalline, showing minute shuttle-shaped forms generally densely grouped together. This salt is very stable. Strongly heated, however, on platinum foil, it burns with evolution of sulphurous acid.

Analysis furnished numbers leading to the formula of disulphobenzolate of barium,



The preceding researches establish in two different groups of bodies the existence of a series of bibasic acids, containing 4 equivalents of sulphur, and which, irrespectively of any special view regarding their molecular arrangement, may be represented as formed by the association of the hydrocarbons (corresponding to marsh-gas) of the various groups with 4 equivalents of anhydrous sulphuric acid:—

| | | |
|------------------------|-----------|--------------------|
| Disulphometholic acid | | $C_2H_44SO_3$ |
| Disulphetholic acid | | $C_4H_64SO_3$ |
| Disulphopropiolic acid | | $C_6H_84SO_3$ |
| Disulphobenzolic acid | | $C_{12}H_64SO_3$. |

An acid of analogous composition exists in the naphthalin-series:—

Disulphonaphtholic acid $C_{20}H_8SO_3$,

which was discovered by Berzelius, and subsequently studied by Laurent.

Many of these substances may actually be produced directly from the hydrocarbons by the action of sulphuric acid. On the other hand, chemists are well acquainted with the deportment of olefiant gas under the influence of anhydrous sulphuric acid. The crystalline compound discovered by Magnus, and described by him under the name of Sulphate of Carbyl, whatever its constitution may be, can be considered as a direct combination of olefiant gas with four equivalents of anhydrous sulphuric acid,

Sulphate of Carbyl $C_4H_4SO_3$.

It can scarcely be doubted that all the other hydrocarbons of the series $C_{2n}H_{2n}$, propylene, butylene, amylene, &c., will furnish homologous substances.

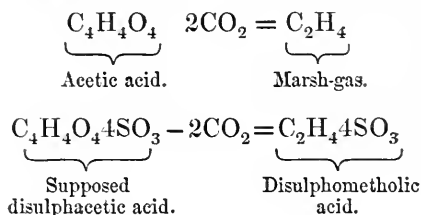
Sulphate of carbyl, when submitted to the action of water, assimilates two equivalents, and is converted into a bibasic acid (ethionic), $C_4H_4SO_3 + 2HO = C_4H_6O_4SO_3$, which accordingly may be viewed as an association of alcohol with four equivalents of anhydrous sulphuric acid. Terms analogous to ethionic acid are sure to be found when the study of the homologues of sulphate of carbyl shall be taken up by chemists.

The production of disulpho-compounds of perfectly similar composition, from substances belonging to such different groups of bodies as the hydrocarbons, homologous and analogous to marsh-gas, as ethylene, and as alcohol, suggested the possibility that the substances observed might be but individual examples of a far more general mode of formation. It became, in fact, probable that all organic bodies, capable of uniting with the elements of two equivalents of anhydrous sulphuric acid, might, under favourable circumstances, be induced to assimilate two additional equivalents of anhydrous sulphuric acid, and thus furnish terms belonging to the class of disulpho-compounds.

The hope of arriving at a more general interpretation of our observations induced us to institute some further inquiries, the result of which we will briefly append.

The first question which naturally suggested itself, was the examination of the deportment of the sulpho-acids derived from acetic, propionic, butyric, benzoic acid, &c., under the influence of an excess of sulphuric acid. To take acetic acid as an illustration, Is sulphacetic acid, $C_4H_4S_2O_{10} = C_4H_4O_4 \cdot 2SO_3$, capable of combining with two additional equivalents of sulphuric acid in order to furnish the compound $C_4H_4S_4O_{16} = C_4H_4O_4 \cdot 4SO_3$? The experiments hitherto detailed contain no evidence against this assumption.

tion. It appeared to us extremely probable that sulphacetic acid, when submitted to the action of sulphuric acid, is converted into disulphacetic acid, which, losing carbonic acid, produces disulphometholic acid, the deportment of disulphacetic under the influence of heat being closely analogous with that of acetic acid,



We have endeavoured to decide this question by experiment; but on account of the greater stability of the benzoic molecule, we have preferred to trace the intermediate acid in the benzoyl-series.

Sulphobenzoic acid, obtained from the acid barium-salt, was evaporated to dryness and heated until it attained the point of quiet fusion. When cold, the acid was coarsely powdered, and mixed with rather more than its own bulk of crystallized sulphuric acid.

It was then heated in a water-bath to a temperature below that at which gases are disengaged. This appeared to be just below 85°C . The substances were kept in contact at this temperature for eight hours. Finally, the mixture was subjected to the heat of boiling water for two hours longer; after which it was treated in the usual way for obtaining the soluble barium-salt.

The salt thus obtained in no manner differed, either in appearance, reaction, or composition, from sulphobenzoate of barium.

Though the above experiments have failed to realize our hopes of producing disulphobenzoic acid, they by no means disprove the existence of this body, and the possibility of producing it under more favourable circumstances. We insist upon this point, on account of the success which has attended our endeavours to trace the existence of disulpho-acids in a perfectly different group of bodies.

We are indebted to M. Gerhardt for the knowledge of a conjugated sulpho-acid, containing an organic base in the place of hydrocarbons, alcohols, acids, &c., which are present in the usual sulpho-acids. Sulphanilic acid, $\text{C}_{12}\text{H}_7\text{NS}_2\text{O}_6$, may be viewed as formed by the association of one equivalent of aniline and two equivalents of anhydrous sulphuric acid.

We were curious to ascertain whether this acid, by assimilating once more the elements of anhydrous sulphuric acid, was capable of becoming disulphanilic acid, $\text{C}_{12}\text{H}_7\text{NS}_4\text{O}_{12}$.

The existence of disulphobenzolic acid, $C_{12}H_6S_4O_{12}$, the barium-salt of which we have described in the preceding pages, together with the formation of an interesting acid lately obtained by M. Hilkenkamp* in the reaction of sulphite of ammonium on dinitrobenzol, appeared to leave no doubt regarding the existence of a disulphanilic acid. In fact, M. Hilkenkamp's dithiobenzolic acid, $C_{12}H_8N_2S_4O_{12}$, is most intimately connected with the acid we were in search of, as is obvious by a glance at the following Table, in which we have placed a number of known substances in juxtaposition with bodies, ideal at present, but the existence of which can no longer be doubted.

| Hydrocarbons and substitutes. | Sulpho-acids and substitutes. | Disulpho-acids and substitutes. |
|---|---|---|
| $C_{12}H_6$ Benzol. | $C_{12}H_6S_2O_6$ Sulphobenzolic acid. | $C_{12}H_6S_4O_{12}$ Disulphobenzolic acid. |
| $C_{12} \left\{ \begin{array}{c} H_5 \\ NO_4 \end{array} \right\}$ Nitrobenzol. | $C_{12} \left\{ \begin{array}{c} H_5 \\ NO_4 \end{array} \right\} S_2O_6$ Nitrosulphobenzolic acid. | $C_{12} \left\{ \begin{array}{c} H_5 \\ NO_4 \end{array} \right\} S_4O_{12}$ |
| $C_{12} \left\{ \begin{array}{c} H_5 \\ NH_2 \end{array} \right\}$ Phenylamine. Aniline. | $C_{12} \left\{ \begin{array}{c} H_5 \\ NH_2 \end{array} \right\} S_2O_6$ Phenylsulphamic acid. Sulphanilic acid. | $C_{12} \left\{ \begin{array}{c} H_5 \\ NH_2 \end{array} \right\} S_4O_{12}$ Phenyldisulphamic acid. Disulphanilic acid. |
| $C_{12} \left\{ \begin{array}{c} H_4 \\ NO_4 \\ NO_4 \end{array} \right\}$ Dinitrobenzol. | $C_{12} \left\{ \begin{array}{c} H_4 \\ NO_4 \\ NO_4 \end{array} \right\} S_2O_6$ | $C_{12} \left\{ \begin{array}{c} H_4 \\ NO_4 \\ NO_4 \end{array} \right\} S_4O_{12}$ |
| $C_{12} \left\{ \begin{array}{c} H_4 \\ NH_2 \\ NH_2 \end{array} \right\}$ Phenyldiamine. (Semaniline?) | $C_{12} \left\{ \begin{array}{c} H_4 \\ NH_2 \\ NH_2 \end{array} \right\} S_2O_6$ | $C_{12} \left\{ \begin{array}{c} H_4 \\ NH_2 \\ NH_2 \end{array} \right\} S_4O_{12}$ Dithiobenzolic acid. Phenyldisulpho-diamic acid. |

The preceding synopsis, whilst it fixes, we believe, the correct position of dithiobenzolic acid in the benzol-series, exhibits at the same time its close relation to the disulphanilic acid, which we endeavoured to produce, and the formation of which it may at once be stated succeeded without much difficulty.

ACTION OF SULPHURIC ACID UPON ANILINE.

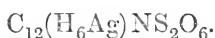
In order to prepare disulphanilic acid, two parts of strong sulphuric acid were mixed with one part of aniline, when heat was freely evolved, sulphate of aniline being thrown down at the same

* Ann. Ch. Pharm. Neue Reihe, B. xix, S. 86.

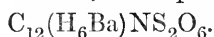
time. On further application of heat the salt redissolved, and as the liquid reached the boiling-point it became very dark in colour, sulphurous acid being freely evolved.

In our first experiment the mixture was kept in full ebullition for ten minutes, and then poured into water after it had partially cooled. A confusedly crystalline mass was produced which was well washed with cold water (in which it is not very soluble), and afterwards recrystallized from hot water.

Sulphanilate of Silver.—A portion of this acid was digested with carbonate of silver. The crystalline silver-salt, obtained by evaporating the solution at a low temperature, was dried at 120° and ignited. The silver-percentage led to the formula of sulphanilate of silver,



Sulphanilate of Barium.—A barium-salt, prepared in the usual way and submitted to analysis by precipitation by sulphuric acid, gave perfectly analogous results, corresponding to the formula



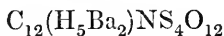
These experiments proved that the acid produced was nothing but M. Gerhardt's well-known sulphanilic acid, the reaction not having gone far enough for the production of the second acid. The treatment with sulphuric acid was therefore resumed. Finely powdered and dry sulphanilic acid, mixed with strong fuming acid to the consistency of a thin paste, was heated in an air-bath to a temperature just approaching that at which sulphurous acid is generated, to 160° and 170° C. This digestion was continued until a portion taken on a glass rod did not solidify on cooling, or give any solid matter when dissolved in a small quantity of water, which happened after the lapse of seven hours, when the mass had the consistency of treacle. It was dissolved in cold water, and separated from a black, almost insoluble matter, which appeared to be somewhat crystalline.

Disulphanilate of Barium.—After saturating with carbonate of barium, the liquid was evaporated to dryness, by which treatment a further separation of the black substance was effected, and the barium-salt was much improved in colour.

If the barium-salt be redissolved and the solution evaporated on the water-bath, a horny substance is formed, which on cooling splits by cracks in all directions; but if the evaporation be completed under the receiver of an air-pump, a mass of microscopic crystals appear, insoluble in alcohol and in ether.

In preparing the new barium-salt, we have found it convenient to precipitate a small portion of the whole liquid by alcohol, and to reject, as retaining generally traces of sulphanilate, the precipitate first formed. Under all circumstances it is very difficult entirely to remove all colouring matter from the solutions of this

salt, which is usually of a pale rose colour. The numbers obtained in the analysis of this salt agree well with the formula of disulphanilate of barium,



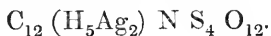
Disulphanilate of barium blackens without inflaming when heated on foil, in which respect it differs from the sulphanilate, which burns with a bright but smoky flame. Heated in close vessels it furnishes a vapour, which sublimes in beautiful crystals, probably of sulphite of aniline, obtained under similar circumstances from sulphanilic acid.

Disulphanilate of barium is attacked by concentrated nitric acid and gives a yellow liquid, which furnishes on evaporation crystals of a very bitter taste; sulphate of barium is formed at the same time.

Disulphanilic Acid is easily produced from a lead-salt. This substance possesses a very acid and pungent taste; it crystallizes with great difficulty, but is insoluble in alcohol which precipitates strong solutions in white grains. This precipitation is assisted by the addition of a little ether. We have not analysed this body, but we have examined in addition,

Disulphanilate of Silver.—The liquid formed by neutralizing a concentrated solution of the acid with carbonate of silver is precipitated cold by the addition of a mixture of equal volumes of alcohol and ether. The salt subsides in colourless crystalline grains; the deposition is much facilitated by rapidly stirring the contents of the beaker with a glass rod. Disulphanilate of silver crystallizes by spontaneous evaporation of the aqueous solution in small laminæ which blacken and deposit a black powder when boiled with water.

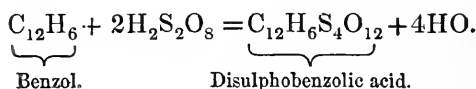
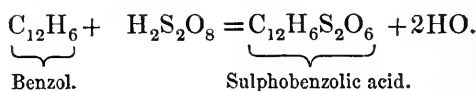
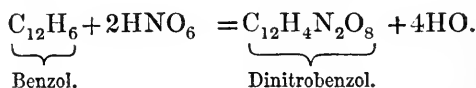
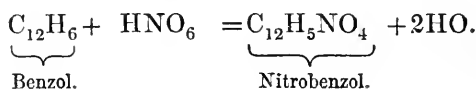
The formula of disulphanilate of silver is—



The researches detailed in the preceding paragraphs may serve to characterize more fully a class of compounds of which only a few terms, isolated and scattered in widely different groups, had been previously observed. The only disulpho-acids hitherto known, were Berzelius and Laurent's disulphonaphtholic acid and Magnus's ethionic (disulphethylic) acid, and lastly, dithiobenzolic (phenyl-disulphodiamic) acid, recently discovered by M. Hilkenkamp. To these this memoir adds five new acids belonging to several of the most important series of compounds.

| | | | | | |
|------------------------|-------|-----------------|--------------|----------------|-------------------|
| Disulphometholic acid | . . . | C_2 | H_4 | S_4 | O_{12} . |
| Disulphetholic acid | . . . | C_4 | H_6 | S_4 | O_{12} . |
| Disulphopropionic acid | . . . | C_6 | H_8 | S_4 | O_{12} . |
| Disulphobenzolic acid | . . . | C_{12} | H_6 | S_4 | O_{12} . |
| Disulphanilic acid | . . . | C_{12} | H_7 | N S_4 | O_{12} . |

Our experiments point out, moreover, the universal occurrence and the general mode of formation of these substances. All organic molecules, particularly in the nascent state, appear to be capable of assimilating the elements of either one or two equivalents of anhydrous acid. The formation of the two groups of acids which are thus produced, presents a great analogy with the production of the nitro-substitutes generated under the influence of nitric acid. All these compounds are generated with elimination of water. In the action of nitric acid and sulphuric acid upon benzol, for instance we have



The analogy of these reactions is obvious.

The action of nitric acid upon organic bodies is by no means limited to the production of nitro-compounds, corresponding to nitrobenzol and dinitrobenzol; frequently additional bodies are formed with elimination of 6, 8, and in a few isolated cases, even of 10 equivalents of water. It is possible that analogous sulpho-compounds may exist; hitherto, however, no substances have been observed in which the assimilation of sulphuric acid has gone further than in the disulpho-acids.

APPENDIX.

During the prosecution of the researches detailed in the preceding paper, our attention was repeatedly called to the substance which M. Liebig has described under the name of *methionic acid*, and which he obtained in the reaction of anhydrous sulphuric acid upon dry ether at low temperatures.* The properties of the barium-salt of this most remarkable acid very closely agree with

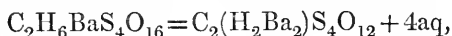
* Liebig, Ann. Ch. Pharm. xiii. 32; xxv. 39. Ann. Ch. Phys. i, 59, 189. Wetherill, Ann. Ch. Pharm. lxvi, 122.

those which we observed in studying disulphometholate of barium, although both appeared different in composition. We were repeatedly inclined to admit and to doubt the identity of the two substances. We have now arrived at the conclusion, that methionic and disulphometholic acid are actually *identical*.

The formula adopted by M. Liebig for the barium-salt is



If we double this formula we arrive at the expression



which represents disulphometholate of barium with 4 equivalents of water of crystallization. Our experiments have actually proved that this salt contains indeed 4 equivalents of water, and that this water is retained at 100°C ., the temperature at which M. Liebig dried his salt before submitting it to analysis.

More recently M. Redtenbacher and M. Wetherill have investigated the same barium-salt, but neither of them appears to have remarked the fact, that this salt loses water between 100° and 200° . M. Redtenbacher analysed a salt which M. Liebig had prepared himself. M. Wetherill examined a salt which he obtained as a secondary product in his researches on sulphate of ethyl.

Although we had no longer any doubt regarding the identity of methionic acid and disulphometholic acid, we considered it desirable to offer a direct experimental proof of our opinion by a comparison of the barium-salt obtained either by M. Liebig's or by M. Wetherill's process with our new barium-compound. We have, therefore, repeatedly prepared methionate of barium both by M. Liebig's and by M. Wetherill's method. By following exactly the plan described by these chemists, we have actually succeeded in obtaining a salt possessing all the characters of disulphometholate of barium. We did not succeed, however, in obtaining by either of these processes a great quantity of this barium-salt. In both processes, the salt is obviously the product of a secondary reaction.

May 9th, 1856.

Chemical Notices.*

By H. Limpricht.

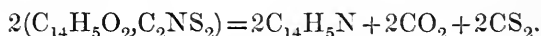
(Continued from page 189.)

4. *On Sulphocyanide of Benzoyl.*

WHEN chloride of benzoyl and sulphocyanide of potassium are mixed in equal numbers of atoms, great heat is evolved, and the odour of sulphuretted hydrogen becomes perceptible; and on distilling the mixture, a slightly coloured liquid passes over, which becomes colourless after a few rectifications, boils at 191° , and possesses all the properties of benzonitrile; its analysis also gives results agreeing with the composition of that body:

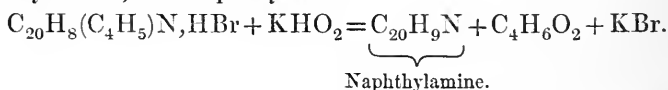
| <i>Benzonitrile.</i> | | Calc. | Found. |
|---|----|-------|--------|
| 14 C . . . | 84 | 81.6 | 81.0 |
| 5 H . . . | 5 | 4.8 | 5.1 |
| N . . . | 14 | 13.6 | 13.4 |
| <hr/> C ₄ H ₅ N . . . | | 100.0 | 99.5 |

In all probability, sulphocyanide of benzoyl is first formed, and is afterwards decomposed in the manner shown by the following equation:

5. *Ethylonaphthylamine*, C₂₀H₈(C₄H₅)N.

When bromide of ethyl is heated for some hours with naphthylamine in an apparatus which allows the condensed bromine-vapours to flow back again,—or when the two bodies are simply placed in contact for some days at ordinary temperatures, reddish, nodular crystals are formed, consisting of hydrobromate of ethylonaphthylamine, which may be obtained colourless by a few recrystallizations. The colourless crystals, after drying over sulphuric acid, yielded in two experiments 31.5 and 31.7 p.c. bromine, the formula C₁₀H₈(C₄H₅)N, HBr requires 31.7.

Potash added to the solution of this salt separates, not ethylonaphthylamine, but naphthylamine:

6. *Preparation of Benzamic Acid.*

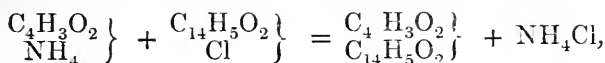
The action of ferrous acetate on nitro-compounds appears to be always analogous to that of sulphide of ammonium; and accord-

* Ann. Ch. Pharm. xeviii, 117.

ingly, nitrobenzoate of ethyl heated with metallic iron and acetic acid is converted into benzamate of ethyl. The acid separated from the latter by alcoholic potash was converted into a barium-salt, and gave 37.3 p.c. barium, the formula of benzamate of barium requiring 37.4 p.c.

7. *A compound produced from Aldehyde-Ammonia and Chloride of Benzoyl.*

With the view of obtaining compounds analogous to the so-called alcohol-radicals by double decomposition between the aldehyde-ammonias and the chlorides of the acid radicals, ordinary aldehyde-ammonia was brought in contact with chloride of benzoyl; but, instead of the expected compound $\left. \begin{smallmatrix} C_4H_3O_2 \\ C_{14}H_5O_2 \end{smallmatrix} \right\}$, which might be formed in the manner represented by the equation



a body was formed having the composition, $C_{32}H_{16}N_2O_4$; its mode of formation, however, is not at present intelligible.

For the preparation of this substance, finely pulverized aldehyde-ammonia must be added to chloride of benzoyl by very small portions, so as to avoid heating, and the consequent formation of brown resinous products, the additions being continued till the mass has become solid; the mixture must then be left to stand for some hours, washed with water to remove sal-ammoniac, and with carbonate of soda to remove benzoic acid. The residue is dissolved in hot alcohol, and the solution on cooling deposits long delicate needles united in concentric groups; the mother-liquor yields the same crystals to the last drop.

The compound is insoluble in water, dissolves sparingly in alcohol and ether in the cold, but freely with the aid of heat; melts when heated, and sublimes at a higher temperature, partly without decomposition.

Heated with potash-ley, it is decomposed very slowly, giving off ammonia, and depositing a brown resin, like resin of aldehyde; and the potash-solution contains benzoic acid.

It is not altered by heating with peroxide of lead and water; but if a little sulphuric acid is added, aldehyde is evolved, and the liquid filtered while hot deposits crystals of benzamide.

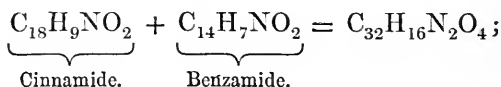
When the compound is stirred up with water through which nitrous acid is passed, aldehyde is also formed together with benzamide.

Strong sulphuric acid heated with the compound dissolves it, forming a brown solution; on addition of water, a brown resin,

separates out, and the liquid filtered while hot yields crystals of benzoic acid.

When it is boiled, in alcoholic solution or suspended in water, with carbonate of silver or mercuric oxide, neither of these compounds is either dissolved or reduced. The alcoholic solution is not precipitated by nitrate of silver, even with addition of ammonia.

The rational formula of the substance cannot at present be determined. It may be observed, however, that the empirical formula above given contains the elements of benzamide and cinnamide :



and that the numbers found by Schwartz for hipparaffin, viz., 71.4 C, 6.1 H, and 10.5 N agree nearly with the composition of the new compound, which gives, as a mean, 71.7 C, 6.3 H, and 10.4 N.

On a New Mode of Formation of Hydride of Benzoyl.*

By H. Kolbe.

CHEMISTS are now pretty generally agreed that benzoic acid, chloride of benzoyl, cyanide of benzoyl, &c., should be regarded as compounds of the oxygenated radical, $C_{14}H_5O_2$ or $(C_{12}H_5)C_2O_2$. Respecting the constitution of bitter-almond oil, however, there is still some doubt; some being inclined to regard that body as $C_{14}H_5O_2, H$, others as $C_{14}H_5O, HO$. If the former view be correct, it is to be expected that this body will be formed by the action of nascent hydrogen on the chloride or cyanide of benzoyl. Experiments in this direction have indeed been already made by Chiozza,† who finds that when chloride of benzoyl is poured upon hydride of copper (Cu_2H), subchloride of copper is formed, and the liquid, after the excess of chloride of benzoyl has been removed by water, exhibits a distinct odour of bitter-almond oil. The quantity obtained, however, was not sufficient for complete identification.

The action of hydrochloric acid and zinc on the chloride of benzoyl is not adapted for the production of the hydride, because the chloride is too quickly resolved into benzoic and hydrochloric acids, to allow the nascent hydrogen to act upon it; but the cyanide,

* Ann. Ch. Pharm. xcvi. 345.

† Ann. Ch. Pharm. lxxxv. 232.

which is much less rapidly decomposed by water than the chloride, gives better results.

When pure crystallised cyanide of benzoyl is mixed in a tubulated retort, with hydrochloric acid, and heated till it melts, and pieces of granulated zinc are introduced from time to time, a rapid evolution of gas takes place at first ; but this soon ceases, especially if the liquid be shaken, so as to bring the cyanide of benzoyl, which floats on the surface, in contact with the metal. If the addition of zinc be continued, the colourless cyanide of benzoyl begins, after a while, to assume a yellow tint where it adheres to the metal. At the same time a strong odour of hydrocyanic acid is evolved, and, as the decomposition of the cyanide of benzoyl proceeds, the odour of bitter-almond oil likewise becomes distinctly perceptible. To effect the complete resolution of the cyanide of benzoyl into hydrocyanic acid and hydride of benzoyl, a considerable quantity of zinc is required. Towards the end of the operation, the zinc becomes covered with a dirty yellow, greasy mass, which ultimately, when all the oil-drops have disappeared from the surface of the chloride of zinc solution, completely envelops the metal.

When this greasy substance is separated from the supernatant acid saline solution, which contains but a small quantity of benzoic acid, and then heated with excess of ordinary potash-ley, it is decomposed, and converted into yellowish-red oily drops, which diffuse the pure odour of bitter-almond oil, the pieces of zinc, at the same time, appearing with a bright metallic surface. On distilling this alkaline mass, pure hydride of benzoyl first passes over into the receiver in considerable quantity, in the form of an oily body, together with the water ; at a later stage of the process, the milky distillate contains benzoin, the greater part of which, however, is contained in the alkaline residue. The oily distillate, after being separated from the water by a pipette, further dehydrated by chloride of calcium, and distilled in a bulb-apparatus like that used by Bunsen for the preparation and purification of cacodyl, was perfectly transparent and colourless ; exhibited the composition and properties of bitter-almond oil ; and solidified to a crystalline mass with bisulphite of soda.

The turbid alkaline liquid remaining in the retort and containing benzoin, was poured, when cold, from the metallic zinc and filtered. The filtrate yielded, on addition of hydrochloric acid, a somewhat copious precipitate of benzoic acid, and, at the same time, hydrocyanic acid was set free. The dirty grey substance remaining on the filter, when likewise treated with hydrochloric acid, left impure benzoin, which, after recrystallisation from boiling alcohol, exhibited the composition and properties of the pure substance.

To prevent the transformation of the hydride of benzoyl into benzoin, and to determine how much hydride of benzoyl can be

obtained, under the most favourable circumstances, from a given quantity of the cyanide, another portion (obtained from 30 grms. of cyanide of benzoyl) of the yellow, greasy mass surrounding the pieces of zinc, was distilled with excess of milk of lime, after addition of protosulphate of iron; but not a trace of hydride of benzoyl was obtained. It seems probable, therefore, that the yellow mass does not contain the hydride of benzoyl in the form of a mere mixture; but that it is a chemical compound, perhaps the oily compound of hydride of benzoyl and hydrocyanic acid described by Völekel*, made thicker in the present instance by admixture of benzoic acid. This compound, which is decomposed by potash, appears to resist the action of hydrate of lime.

The conversion of cyanide of benzoyl into hydrocyanic acid and hydride of benzoyl likewise takes place, though much more slowly, by continued gentle heating with metallic mercury and hydrochloric acid (better and more quickly, perhaps, in a sealed tube).

On some Compounds of Benzoyl.†

By Carl Voit.

THE compounds of benzoic acid with bases have not hitherto been much studied, only the silver-salt having been analysed by Chancel, and a few compounds of benzoic acid with other acids, in which it appears to play the part of a base, having been studied by Gerland. The behaviour of binitrobenzoic acid with sulphuretted hydrogen was likewise unknown, and it could not be determined beforehand, whether both equivalents of hyponitric acid, or only one, would be replaced by amidogen. The following experiments were undertaken to supply these deficiencies.

Nitrobenzoic acid was prepared by adding fused benzoic acid, in small portions, to a mixture of 2 pts. concentrated sulphuric acid, 1 pt. nitric acid (sp. gr. 1.5), and heating the mixture gently for about half an hour; no binitrobenzoic acid is thereby produced, that acid being, in fact, much less easy to obtain than is commonly supposed; but on adding water to the mixture, nitrobenzoic acid is precipitated in white flakes.

When chloride of benzoyl is dropped into the mixture of sulphuric and nitric acid, the liquid becomes heated, and gives off chlorine, together with another gas which attacks the eyes powerfully; water then throws down white flakes, which were found, by analysis, to be pure nitrobenzoic acid.

* Pogg. Ann. lxii. 444.

† Ann. Ch. Pharm. xcvi. 100.

The nitrobenzoic acid was transformed by the usual method of boiling with sulphide of ammonium, into *amidobenzoic* or benzamic acid;* and, on adding strong hydrochloric acid to the liquid, after it had been decanted from the precipitated sulphur and evaporated, hydrochlorate of amidobenzoic acid was precipitated in needles united in nodular groups; this compound served for the preparation of the following salts:—

Amidobenzoate of Soda, $C_{14}H_4Na(NH_2)O_4$ (at 100°).—From the hot concentrated solution of the baryta-salt, the baryta was precipitated by an equivalent quantity of sulphate of soda, and the filtrate evaporated to dryness. This soda-salt is so very soluble in water, that it is difficult to get it well crystallised. The concentrated solution was therefore mixed with absolute alcohol, and the resulting white crystalline magma pressed between paper, and dried at 100° . Under the microscope it appeared to consist of needle-shaped crystals.

| | Calculated. | Found. |
|----------------|-------------|--------|
| Soda | 19.50 | 19.13 |

Amidobenzoate of Baryta, $C_{14}H_4Ba(NH_2)O_4$ (at 100°).—The aqueous solution of hydrochlorate of amidobenzoic acid was neutralised with carbonate of baryta, and the hot filtrate evaporated over the water-bath; at a certain degree of concentration, it deposits large pale reddish prisms, which cannot be completely decolorised, even by repeated crystallisation, with addition of animal charcoal, but yield a pure white powder.

| | | Calc. | Found. |
|----------------------------|-------|--------|--------|
| 14 C | 84.0 | 41.07 | 41.12 |
| 6 H | 6.0 | 2.93 | 3.51 |
| Ba | 68.5 | 33.50 | 33.20 |
| N | 14.0 | 6.84 | |
| 4 O | 32.0 | 15.66 | |
| <hr/> | | <hr/> | |
| $C_{14}H_4Ba(NH_2)O_4$. . | 204.5 | 100.00 | |

Amidobenzoate of Strontia, $C_{14}H_4S_2(NH_2)O_4 + 2aq.$ — The aqueous solution of the baryta-salt was precipitated with sulphuric acid; and the filtrate mixed with hydrate of strontia, till a slight alkaline reaction was produced, and evaporated. It then deposited prisms having a faint reddish colour, but becoming white by recrystallisation. They dissolve very readily in water, slowly in alcohol, and give off their water of crystallisation at 100° .

| | Calc. | Found. |
|--------------------|-------|--------|
| Water | 9.10 | 8.78 |
| Strontia | 28.81 | 28.58 |

* The author objects to the ordinary name benzamic acid, because it is only the radicals of bibasic acids which can form acids to which the termination *amic* can be properly applied.

Amidobenzoate of Lime, $C_{14}H_4Ca(NH_2)O_4$.—Hydrochlorate of benzoic acid was boiled with milk of lime, and the filtrate evaporated. The concentrated liquid soon deposited delicate white needles, which turned red on exposure to the air; they were once recrystallised from hot alcohol, then quickly pressed and dried at 100° .

| | Calc. | Found. |
|------------|-------|--------|
| Lime . . . | 17.95 | 17.61 |

Amidobenzoate of Magnesia, $C_{14}H_4Mg(NH_2)O_4 + 7aq.$ — By double decomposition between the baryta-salt and sulphate of magnesia, this salt is obtained in large, transparent, six-sided prisms, with oblique truncation-face; it decomposes quickly on exposure to the air.

| | Calc. | Found. | |
|----------------|-------|--------|-------|
| Water . . . | 29.86 | 29.36 | |
| Magnesia . . . | 13.51 | 13.65 | 13.07 |

Binitrobenzoic acid was obtained by Cahours, by gently heating benzoic acid for an hour, with a mixture of sulphuric and nitric acid. Voit obtained, by this process, only nitrobenzoic acid, or a mixture of that acid with binitrobenzoic, and found it necessary to boil for six hours longer, with sulphuric and nitric acid, in order to convert the nitrobenzoic into binitrobenzoic acid. At the beginning of the operation, the evolution of nitrous acid is so violent that, unless the heat is well regulated, the mixture is very apt to froth over; but at length a point is attained, when red fumes are no longer evolved. If the liquid be then left to cool, the binitrobenzoic acid separates almost completely in shining crystals; if the heat be longer continued, vapours are evolved which excite coughing; the liquid assumes a darker colour; and the binitrobenzoic acid, which separates on cooling, is likewise coloured. Binitrobenzoic acid is much less soluble in water, either hot or cold, than nitrobenzoic acid: carbonate of soda dissolves it, forming a red solution. By boiling with water and carbonate of baryta, the baryta-salt was obtained, and settled down from the hot filtrate on cooling in yellowish crystalline nodules. It yielded by analysis, 27.35 and 27.17 p.c. baryta, agreeing with the formula $C_{14}H_3Ba(NO_4)_2O_4$, which requires 27.37.

Binitrobenzoate of ethyl is easily produced, by heating binitrobenzoic acid with alcohol and sulphuric acid, and forms oily drops, which solidify on cooling. It dissolves readily in hot, very sparingly in cold alcohol, so that the alcoholic solution, when filtered hot, solidifies to a magma consisting of silky needles. On attempting to prepare biamidobenzamide, by digesting this ether with sulphide of ammonium, sulphur was deposited in considerable quantity, and the filtrate, when evaporated, yielded a crystalline

mass, which, however, could not be obtained sufficiently pure for analysis.

On the other hand, binitrobenzoate of ethyl is readily converted into *binitrobenzamide* by digesting it for several days with alcoholic ammonia, which dissolves it with blood-red colour, and after concentration deposits the amide in prisms and laminæ having a faint yellowish colour and fatty lustre. Binitrobenzamide dissolves sparingly in cold, somewhat more readily in hot water, forming a solution which has a bitter taste and neutral reaction. It melts at 183° , and decomposes at a higher temperature without subliming. The ammoniacal solution forms no precipitate with nitrate of silver.

| <i>Binitrobenzamide.</i> | | Calc. | Found. |
|-----------------------------|----|-------|--------|
| 14 C | 84 | 39·81 | 40·87 |
| 5 H | 5 | 2·37 | 2·88 |
| 2 NO ₂ | 92 | 43·60 | |
| N | 14 | 6·63 | 6·90 |
| 2 O | 16 | 7·59 | |

| | | |
|-----|---|--------|
| N { | C ₁₄ H ₃ (NO ₂) ₂ O ₂ | |
| | H | 211 |
| | H | |
| | | 100·00 |

To convert the binitrobenzoic acid into *Biamidobenzoic* acid, sulphuretted hydrogen was passed continuously through the hot ammoniacal solution; the solution filtered from sulphur, evaporated over the water-bath, supersaturated with hydrochloric acid, and again filtered hot: the filtrate after a while deposited green crystals of hydrochlorate of biamidobenzoic acid.

Biamidobenzoic acid, obtained by digesting the aqueous solution of the sulphate with carbonate of baryta, and evaporating the filtrate, first over the water-bath, and afterwards over sulphuric acid, forms small, greenish, acuminate crystals, which dissolve readily in water, alcohol, and ether; have no taste and no reaction upon vegetable colours; melt and blacken at about 195° ; and cannot be sublimed.

It is remarkable that biamidobenzoic acid does not combine with bases, but forms well crystallized compounds with acids, whence the name of acid is not very appropriate for it. In this respect, it exhibits the behaviour which is seen so remarkably in aniline, viz., that the substitution-products retain in general the character of the compound from which they are derived; but, nevertheless, the substance which enters does not completely lose its chemical character, but impresses that character on the substitution-product, the more strongly as the number of hydrogen-atoms replaced by it is greater. Benzoic acid is a strong acid; the introduction even of one atom of the basic substance, amidogen, causes it already to exhibit basic properties, for amidobenzoic acid

unites with acids as well as with bases; while with the second atom of amidogen, the acid qualities completely disappear, the product biamidobenzoic acid forming salts only with acids.

Hydrochlorate of Biamidobenzoic Acid, $C_{14}H_4(NH_2)_2O_4, 2HCl$.—The impure compound obtained in the preparation of biamidobenzoic acid, is not easily purified by recrystallization; a pure salt is more easily prepared by mixing the solution in a small quantity of water with strong hydrochloric acid; in that case, either white needles are immediately deposited, or a flocculent precipitate is first produced which afterwards changes to the same needles. Should the salt be not yet perfectly pure, the operation must be repeated. Hydrochlorate of biamidobenzoic acid is very soluble in water, alcohol, and ether; the aqueous solution decomposes on exposure to the air, depositing black flocks. The dry compound melts when heated, then decomposes, and yields a sublimate of sal-ammoniac. For analysis, the salt, after being pressed between paper, was dried, first over sulphuric acid, then at 60° .

| | Calc. | Found. | |
|------------------|-------|--------|-------|
| Chlorine | 31.55 | 31.02 | 31.10 |

Bichloride of platinum does not form any precipitate in the aqueous solution, even on addition of alcohol and ether; but when the mixture is left to evaporate over sulphuric acid, it deposits brown crusts, which after drying yield a greyish-white powder. Its composition appears to be $C_{14}H_4(NH_2)_2O_4, 2HCl, PtCl_2$; for it yielded 24.83 p.c. platinum, and the formula requires 25.01 p.c. If it were analogous to the platinum-salts of other bases which saturate 2 equivalents of acid (*e.g.*, quinine, cinchonine), it would contain 2 eq. $PtCl_2$.

Sulphate of Biamidobenzoic acid, $C_{14}H_4(NH_2)_2O_4, S_2H_2O_8$.—The hydrochlorate was dissolved in dilute sulphuric acid and the solution concentrated; the still brownish tables and laminae which separated, were obtained nearly colourless by recrystallization from alcohol. They dissolve readily in water, somewhat less in alcohol; the solutions decompose very readily, and appear brownish-yellow by transmitted, grass-green by reflected, light.

Crystals dried over Sulphuric acid.

| | | | Found | |
|-------------------------------------|-----|--------|-------|-------|
| 14 C | 84 | 33.60 | 34.33 | 33.55 |
| 10 H | 10 | 4.00 | 4.65 | 4.93 |
| 2 N | 28 | 11.20 | 11.29 | 10.94 |
| 6 O | 48 | 19.20 | | |
| 2 SO_3 | 80 | 32.00 | 32.25 | 32.68 |
| <hr/> | | | | |
| $C_{14}H_4(NH_2)_2O_4, S_2H_2O_8$. | 250 | 100.00 | | |

Nitrate of Biamidobenzoic acid.—Obtained by decomposing

the sulphate with nitrate of baryta; separates in dark-coloured crystals.

Acetate of Biamidobenzoic acid, was prepared by precipitating the sulphate with acetate of baryta. The solution became decomposed during evaporation, and deposited a brown powder; but by further evaporation of the filtered liquid, brownish prisms were obtained.

Oxalate of Biamidobenzoic acid forms brown needles, which are obtained by evaporating the hydrochlorate with oxalic acid.

Biamidobenzoic acid was heated to 100° in a sealed tube with iodide of ethyl, with the view of obtaining biamidobenzoate of ethyl; the mass became solid; but on addition of hydrochloric acid to the aqueous solution, white needles were obtained, which proved to be nothing but hydrochlorate of biamidobenzoic acid.

By decomposing biamidobenzoic acid in hot aqueous solution with nitrous acid, which, according to Gerland, converts amidobenzoic into oxybenzoic acid, only a red, resinous, uncrystallizable mass was obtained, although the passage of the gas was continued for several days.

On some Constituents of Opium*.

By T. Anderson.

THE following experiments, which are a continuation of Dr. Anderson's researches upon opium already reported in this Journal (v, 257; viii, 283), relate chiefly to meconine, its identity with opianyl, and various substitution-products of that substance.

Meconine.—The mother-liquor from which narceine (v. 258) had crystallized out, yielded after being concentrated and left at rest, nothing but granular crystals of sal-ammoniac. To obtain meconine from this liquid, it was mixed in large bottles, with $\frac{1}{2}$ of its bulk of ether; the bottles tightly corked, left to stand in a warm place at about 26° C., and frequently shaken; the ethereal layer then separated; and this treatment several times repeated with fresh ether. The extracts obtained with the first portions of ether, left, after the ether had been distilled off, a brown syrupy residue which yielded no crystals, even after standing for several days; the extracts with the latter portions of ether often left residues in which crystals formed after standing. On adding water to these residues, a viscid substance of the consistence of turpentine separated out; and this substance when treated with hydrochloric acid partly dissolved, while the undissolved portion was converted into a dark grey crystalline powder. The latter was impure meconine;

* Ed. Phil. Trans. xxi, [1], 204. Ann. Ch. Pharm. xeviii, 44.

the hydrochloric acid solution contained papaverine. The meconine was separated, by solution in boiling water, from an indifferent resinous body; and the solution on cooling deposited the meconine in yellowish needle-shaped crystals, which were further purified by recrystallization with addition of animal charcoal.

Pure meconine crystallizes from its aqueous solution in white shining needles. It dissolves in 22 times its weight of boiling water, and in 700 times its weight of water at 15.5 C. (60° F.). It is likewise soluble in alcohol and ether. Has a bitter taste. Melts at 110° C. in the dry state; at 77° under water; when carefully raised to a higher temperature, it volatilizes without residue, and sublimes in beautiful crystals. It does not appear to dissolve in alkaline liquids more readily than in water. Does not combine with metallic oxides; is not precipitated by subacetate of lead. Anderson's analyses of meconine agree nearly with those of Couerbe* and Regnault†, when the latter are calculated according to the atomic weights now adopted, and lead to the formula $C_{10}H_5O_4$ or $C_{20}H_{10}O_8$, which latter Anderson also found for opianyl‡, the substance obtained by the action of nitric acid upon narcotine.

| <i>Meconine.</i> | | Calc. | Found. | |
|---------------------------|-----|--------|--------|--------|
| 20 C . . . | 120 | 61.85 | 61.40 | 61.50 |
| 10 H . . . | 10 | 5.15 | 5.12 | 5.13 |
| 8 O . . . | 64 | 33.00 | 33.48 | 33.37 |
| <hr/> $C_{25}H_{10}O_8$. | | 100.00 | 100.00 | 100.00 |

Meconine and opianyl are likewise identical in properties. Sulphuric acid produces with the former, even in the cold, a colourless solution which assumes a deep purple colour when heated; water added to this solution turns it brown, and separates a dark brown precipitate, which dissolves with red colour in alcohol. Of the two names given to this substance, Anderson gives the preference to *Opianyl*.

Action of Nitric acid upon Opianyl.—Opianyl dissolves abundantly in cold concentrated nitric acid; on heating the liquid, red vapours are evolved in small quantity. The solution diluted with water deposits bulky crystals, which may be purified by washing and recrystallization from boiling alcohol. *Nitropianyl* thus prepared forms white needles and prisms. It dissolves but sparingly in cold, somewhat more freely in boiling water; much more readily in boiling alcohol; dissolves also in ether. All these solutions are colourless and neutral to test-paper. Nitropianyl melts at 160° C., forming a transparent liquid, which solidifies in a crystalline mass on cooling. Heated in small quantities on platinum-foil, it volatilizes without decomposition, leaving only a small carbonaceous

* Ann. Ch. Pharm. xvii, 167.

† Ann. Ch. Pharm. xxix, 314.

‡ Ann. Ch. Pharm. lxxxvi, 191.

residue; but when heated in a small glass-tube, it decomposes suddenly, and leaves a bulky, porous, carbonaceous residue. It is not precipitated by metallic salts. It does not dissolve more abundantly in cold solution of potash or ammonia than in pure water; but at the boiling heat, it dissolves in considerable quantity, and with decomposition, forming a yellow liquid which does not deposit anything on cooling, or on addition of hydrochloric acid. It is insoluble in hydrochloric acid; dissolves in cold strong nitric acid; and separates out in crystalline flakes when the solution is diluted. The crystals of nitropianyl immediately assume a yellow colour when acted upon by strong sulphuric acid, and dissolve to a red liquid when heated. The composition of nitropianyl is $C_{20}H_9(NO_4)O_8$; the same formula was assigned by Couerbe to his hyponitromeconic acid, which, however, differs from Anderson's nitropianyl in certain properties, and, according to Anderson, is not obtained by the process given by Couerbe.

| <i>Nitropianyl.</i> | | | Calc. | Found. |
|----------------------------|-----------|-----|-------|--------|
| 20 C | | 120 | 50.20 | 50.11 |
| 9 H | | 9 | 3.76 | 3.92 |
| N | | 14 | 5.85 | |
| 12 O | | 96 | 40.19 | |
| $C_{20}H_9(NO_4)O_8$. . . | | | 239 | 100.00 |

Action of Chlorine upon Opianyl.—When chlorine gas is passed into a cold-saturated aqueous solution of opianyl, crystals of *Chloropianyl* soon separate in considerable quantities; this compound may also be obtained by passing dry chlorine over fused opianyl.—Chloropianyl purified by recrystallization from alcohol, forms colourless needles which are nearly insoluble in cold water; dissolve somewhat more easily in boiling water; abundantly in alcohol and ether. Alkaline liquids do not dissolve more of it than water, and do not extract chlorine from it; nitric acid dissolves it with red colour, and decomposes it when heated; strong sulphuric acid dissolves it in the cold, and the solution when heated assumes a greenish-blue colour, and on subsequent addition of water, deposits brown flakes soluble with a red colour in alkalis. Chloropianyl melts at $175^\circ C.$, and sublimes without decomposition at a higher temperature. The properties of chloropianyl are the same, whether it is obtained from opianyl which has been prepared from narcotine, or from opianyl obtained directly from opium.

| <i>Opianyl.</i> | | | Calc. | Found. | | |
|------------------|-----|-------|-------|--------|--------|-------|
| 20 C | . . | 120.0 | 52.51 | 52.40 | 52.35 | 52.60 |
| 9 H | . . | 9.0 | 3.93 | 4.32 | 4.21 | 4.20 |
| Cl | . . | 35.5 | 15.53 | 15.17 | | |
| 8 O | . . | 64.0 | 28.03 | 28.11 | | |
| $C_{20}H_9ClO_8$ | | | 228.5 | 100.00 | 100.00 | |

Couerbe describes, as the product of the action of chlorine upon meconine, a resinous substance which Anderson believes to be bichloropianyl.

Action of Bromine on Opianyl.—When bromine-water is gradually added to an aqueous solution of opianyl, crystals gradually separate, consisting of *Bromopianyl*, which may be purified by recrystallization. The compound then forms colourless needles, which dissolve sparingly in water, abundantly in alcohol and ether. *Bromopianyl* melts at 167° C. In its properties it closely resembles chloropianyl.

| <i>Bromopianyl.</i> | | Calc. | Found. |
|---|-----|--------|--------|
| 20 C | 120 | 43·95 | 43·81 |
| 9 H | 9 | 3·29 | 3·40 |
| Br | 80 | 29·30 | 29·21 |
| 8 O | 64 | 23·46 | 23·58 |
| <hr/> C ₂₀ H ₉ BrO ₈ | | 100·00 | 100·00 |

Action of Chloride of Iodine upon Opianyl.—Iodine does not act upon opianyl, either in alcoholic solution or in the solid form. An iodated substitution-product is, however, obtained by adding chloride of iodine to an aqueous solution of opianyl, and leaving the liquid in a warm place for some days; long crystals of *Iodopianyl* are then formed, somewhat contaminated by free iodine separated at the same time. *Iodopianyl* recrystallized from boiling alcohol forms colourless needles, which are scarcely soluble in water, but dissolve more freely in alcohol and in ether. It melts at 112° C., forming a liquid which is colourless at first, but afterwards turns brown; at a higher temperature, it decomposes with volatilization of iodine. Nitric acid likewise decomposes it with separation of iodine. Sulphuric acid dissolves it, and the solution assumes a dark colour when heated.

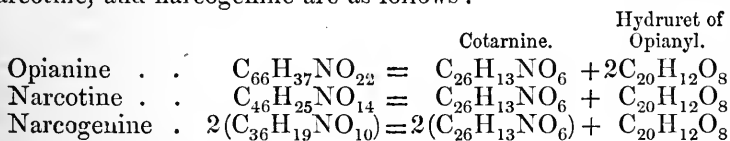
| <i>Iodopianyl.</i> | | Calc. | Found. |
|--|-------|--------|--------|
| 20 C | 120·0 | 37·48 | 37·16 |
| 9 H | 9·0 | 2·81 | 2·96 |
| I | 127·1 | 39·70 | 39·48 |
| 8 O | 64·0 | 20·01 | 20·40 |
| <hr/> C ₂₀ H ₉ IO ₈ | | 100·00 | 100·00 |

Action of Sulphuric acid and Peroxide of Lead upon Opianyl.—When opianyl is gently heated with peroxide of lead and sulphuric acid, carbonic acid is evolved, and an amorphous substance remains in solution. The reaction was not further investigated, in consequence of deficiency of material; the author expected to find opianic and hemipinic acids among the products of the oxidation.

The identity of meconine, which exists ready formed in opium, with opianyl, an artificial product obtained from narcotine, may furnish a starting point in the examination of the relations which

exist between the several constituents of opium. It has long been observed, that those proximate principles of a plant which occur together frequently exhibit a certain similarity in their composition or origin. Thus quinine and cinchonine, which differ only in the number of oxygen-atoms, may be compared with different oxides of the same metal; and again, of the two bases which occur in the seeds of *Peganum Harmala*, the one may be converted into the other by the action of oxidizing agents. Many cases may also be cited in which the formulæ of two simultaneously occurring bases agree in the amounts of certain of their constituents. Thus morphine and codeine differ only by C_2H_2 , like two homologous substances, although they do not exhibit that degree of similarity in their properties which is generally found in homologous compounds. Thebaine, $C_{38}H_{21}NO_6$, and codeine, $C_{36}H_{21}NO_6$, differ by $2C$; thebaine, and papaverine, $C_{40}H_{21}NO_8$, by C_2O_2 ; narceine, $C_{46}H_{29}NO_{10}$, and narcotine, $C_{46}H_{25}NO_{14}$, by $4HO$.

Anderson had formerly remarked* that narcotine may be regarded as a compound of cotarnine and a hypothetical *hydruret of opianyl*. He thinks it possible that the opianine examined by Hinterberger† may have a similar constitution, and that Hinterberger's analyses may be made consistent with the formula $C_{66}H_{37}NO_{22}$. In that case, the relations between opianine, narcotine, and narcogenine are as follows :



Anderson likewise draws attention to a remarkable fact which was brought to light in investigating the action of sulphuric acid upon opianic acid. In this reaction, there is produced a true dye-stuff, which yields with alumina and iron mordants all the colours that are obtained by the use of madder. Now as alizarin, $C_{20}H_6O_6$, differs from opianic acid only by $4Aq.$, Anderson thinks it not improbable that the new colouring matter may be identical with alizarin.

* Chem. Soc. Qu. J., v, 264.

† Ann. Ch. Pharm. lxxvii, 207; lxxxii, 320. Anderson regards the amount of nitrogen in opianine given in the former of these communications as the more correct.

On the Compounds of Stibethyl. *

By W. Merck.

LÖWIG and SCHWEIZER, in their investigation of the compounds of stibethyl,† arrived at the conclusion that the radical $(C_4H_5)_3Sb$ combines with 2 At. of an electronegative body; *e. g.*, the oxide = $(C_4H_5)_3Sb, O_2$; the iodide = $(C_4H_5)_3Sb, I_2$, &c. Similar formulæ were subsequently given by LANDOLT for the compounds of arsentriethyl $(C_4H_5)_3As$, by CAHOURS and RICHE for those of arsentrimethyl, and by BERLÉ for those of stibtriamyl. On the other hand, it was found that arsenbimethyl (cacodyl) $(C_2H_3)_2As$, and arsenbiethyl $(C_4H_5)_2Sb$, as well as arsenethylum $(C_4H_5)_{5/4}As$, and stibethylum $(C_4H_5)_4Sb$, unite with only 1 At. of an electronegative body; and hence arose a doubt as to whether the stibethyl compounds were constituted as above mentioned, or whether they did not rather contain 1 At. hydrogen more, *e. g.*, the iodide = $(C_4H_5)_3Sb, I + HI$ or $(C_4H_5)_3HSb, I_2$. As, however, the percentage composition, according to the more recently proposed formula, differs but little from that deduced from the older one, and therefore the comparative merits of the two cannot be determined by direct analysis, the following experiments on the action of ammonia and of stibethyl on the iodide of stibethyl, were undertaken with the view of deciding the question.

The experiments on the action of ammonia on iodide of stibethyl did not lead to any decisive results. When the solutions of the two bodies in absolute alcohol are mixed, the whole remains clear and colourless; on evaporating the mixture in vacuo over sulphuric acid, the excess of ammonia escapes first, then a salt crystallizes out in regular octohedrons containing 37 per cent. iodine (the iodide of stibtetriethyl presently to be noticed), and at last iodide of ammonium.

The action of stibethyl on the iodide was next tried. One-half of an ethereal solution of stibethyl, prepared out of contact of air, was exactly saturated with iodine, the other half then added, and the mixture left to evaporate in an atmosphere of carbonic acid. There were then formed—first, the octohedral crystals of iodide of stibtetriethyl $(SbAc_3)I$, but afterwards smaller and more soluble crystals, having a different form; these last are regarded by Merck as $(SbAc_3H)I$. [The radical contained in them, *viz.*, $(C_4H_5)_3HSb$, Löwig denotes by the name *stibtetriethylamine*.] The latter crystals yielded from 36·52 to 36·84 per cent. iodine, while the formula $(SbAc_3H)I$, requires 36·92. Now the action of stibethyl on the so-called iodide of stibethyl might be repre-

* J. pr. Chem. lxxvi. 56; Ann. Ch. Pharm., xevii. 329.

† Ann. Ch. Pharm. lxxv. 315. Chem. Soc. Qu. J., v, 69.

sented by one or other of the following equations, according to the formula adopted for the iodide :—

- (1). $(\text{SbAe}_3)\text{I}_2 + \text{SbAe}_3 = 2(\text{SbAe}_3)\text{I}$
- (2). $(\text{SbAe}_3)\text{I}_2 + \text{SbAe}_3 = (\text{SbAe}_4)\text{I} + (\text{SbAe}_2)\text{I}$
- (3). $(\text{SbAe}_3)\text{I}, \text{HI} \left\{ \begin{array}{l} \text{or } (\text{SbAe}_3\text{H})\text{I}_2 \end{array} \right\} + \text{SbAe}_3 = (\text{SbAe}_3\text{H})\text{I} + (\text{SbAe}_3)\text{I}.$

It will easily be seen that the results of the above experiments agree with equation (3), but are inconsistent with (1) and (2). [The formula $(\text{SbAe}_3)\text{I}$, requires 40.26 per cent. iodine.] Hence the formula of iodide of stibethyl must be either $(\text{SbAe}_3)\text{I} + \text{HI}$, or $(\text{SbAe}_3\text{H})\text{I}_2$. This is further proved by several reactions, among which may be cited the momentary formation of the so-called iodide of stibethyl on adding hydriodic acid to a solution of the salt $(\text{SbAe}_3)\text{I}$. Merck does not, however, explain how the compound $(\text{SbAe}_3)\text{I} + \text{HI}$ can be formed by the direct combination of iodine with stibethyl dissolved in alcohol or ether.

COMPOUNDS OF STIBTRIETHYL.

Oxide. SbAe_3O .—This compound is obtained by decomposing the aqueous solution of the iodide with pure and recently precipitated oxide of silver. The filtrate contains in solution a somewhat considerable quantity of oxide of silver, which can only be partially separated by concentration, and must therefore be removed by careful precipitation with dilute hydriodic acid. Hydrochloric acid cannot be used, because it dissolves the oxide in somewhat considerable quantity. The filtered solution is then evaporated, first over the water-bath, and afterwards in vacuo over oil of vitriol.

Thick, syrupy, transparent, colourless mass, which has a slippery feel between the fingers, like very strong potash-ley. It is inodorous; has an intensely bitter and biting taste, and a strong alkaline reaction. It is somewhat volatile, slight fumes being produced when a rod moistened with hydrochloric acid is held over its aqueous solution: it does not, however, diminish perceptibly in weight when kept even for a long time in vacuo over sulphuric acid.

The oxide dissolves readily in water, the solution being attended with considerable rise of temperature. The solution precipitates manganous, ferrous, ferric, cupric, mercuric and lead salts, without dissolving the precipitates in excess. In alumina and zinc salts, it forms white precipitates, soluble in excess.

Oxide of stibtriethyl is a strong base; its salts all dissolve readily in water, but sparingly in alcohol: they have a bitter taste, but no emetic action.

The oxide dissolves readily in alcohol, but sparingly in ether.

The *Sulphide of stibtriethyl* has not yet been obtained in the

separate state. On saturating an alcoholic solution of the oxide with sulphuretted hydrogen and leaving it to evaporate, fine crystals are obtained, which appear to be identical with the so-called sulphide of stibethyl.

Carbonate of Stibtriethyl. $\text{SbAe}_3\text{O}, \text{CO}_2$.—Obtained by decomposing the iodide with carbonate of silver. On evaporating the filtrate over the water-bath, the salt remains in the form of a syrupy mass, without any trace of crystallization.

Sulphate of Stibtriethyl. $\text{SbAe}_3\text{O}, \text{SO}_3$.—Obtained by decomposing the iodide with sulphate of silver. Does not crystallize; but by evaporation, first in the water-bath and then in vacuo over oil of vitriol, it is obtained in the form of a transparent gummy mass, which may be rubbed to a white powder. Deliquesces readily in the air, and dissolves in all proportions in water.

Iodide of Stibtriethyl. SbAe_3I .—Obtained either by exactly saturating the oxide with hydriodic acid, the latter being added in the state of dilute solution, till it produces a permanent cloud, which may then be made to disappear by adding a drop of the oxide; or by the action of ammonia or stibtriethyl on iodide of stibtriethyl and hydrogen, $\text{SbAe}_3\text{I}, \text{HI}$.

Crystallizes very readily. By leaving the ethereal solution to evaporate, large, hard, transparent, colourless, octohedrons or tetrahedrons are obtained, which are inodorous, and have a glassy lustre. They exhibit no trace of decomposition when exposed to the air, even for weeks; they are anhydrous, and suffer no loss of weight in vacuo oil of vitriol. Crystals of the same form are obtained from the aqueous or alcoholic solution.

| Calc. | | | | Found. | | | |
|--|-----|--------|-------|--------|----|-------|-------|
| | | | | a. | b. | c. | d. |
| Sb . . . | 129 | 37.72 | 37.84 | | | | |
| 12 C . . . | 72 | 21.05 | 20.69 | 20.65 | | 20.70 | |
| 15 H . . . | 15 | 4.39 | 4.53 | 4.63 | | 4.52 | |
| I . . . | 126 | 36.84 | 36.68 | 37.70 | | 37.10 | 36.93 |
| <hr/> | | | | | | | |
| $(\text{C}_4\text{H}_5)_3\text{SbI}$. | 342 | 100.00 | 99.74 | | | | |

a and *b* were obtained by the action of ammonia; *c* and *d* by that of stibethyl on the compound, $\text{SbAe}_3\text{I}, \text{HI}$.

An aqueous solution of mercuric bromide added to aqueous iodide of stibtriethyl, forms at first a yellow precipitate, which, however, very soon changes to red, the decomposition being then complete. No doubt the yellow modification of mercuric iodide is formed at first, and afterwards passes into the red. This reaction distinguishes iodide of stibtriethyl from iodide of stibethylum. When the bromide of mercury and iodide of stibtriethyl are mixed in exactly equal numbers of atoms and in the state of alcoholic solution, no precipitate is formed; but on evaporating the liquid,

there remains a slightly yellowish oil, which, indeed, separates as the alcohol evaporates; when this oil is shaken up with water, red iodide of mercury immediately separates out, and bromide of stibtriethyl remains in solution.

Iodide of stibtriethyl is soluble in water, alcohol, and ether.

Bromide of Stibtriethyl. SbAe_3Br .—Obtained by the action of bromide of mercury on iodide of stibtriethyl in alcoholic solution in the manner just mentioned—or better, by adding bromide of barium to the aqueous sulphate of stibtriethyl, as long as a precipitate is formed. The filtrate evaporated over the water-bath, and then in vacuo over oil of vitriol, exhibited traces of crystallization after a week.

Chloride of Stibtriethyl. SbAe_3Cl .—Obtained by decomposing the iodide with corrosive sublimate, the aqueous solutions of the two salts being mixed in exactly equal numbers of atoms; also by adding chloride of stibtriethyl and hydrogen to an aqueous solution of the oxide. Very soluble in water, and crystallizes only from highly concentrated solutions; no definite crystals were obtained. Forms a white, radiated mass, which rapidly absorbs water from the air.

On adding hydrochloric acid to the aqueous solution of this salt, the *acid chloride* $\text{SbAe}_3\text{Cl}, \text{HCl}$, separates in the form of a perfectly colourless liquid, containing 25.16 per cent. chlorine, the formula requiring 24.78 per cent.

The aqueous solution, mixed with bichloride of platinum, does not form any precipitate; but on evaporating the liquid, a dark-coloured oily substance is at length obtained, which, however, has not been further examined.

Nitrate of Stibtriethyl.—*a. Neutral.* $\text{SbAe}_3\text{O}, \text{NO}_5$.—Prepared by decomposing the iodide with nitrate of silver. On evaporating the filtrate, first, in the water-bath, and then over oil of vitriol in vacuo, the whole solidifies in a solid radiated mass, which dissolves very easily in water, but does not deliquesce in the air.

b. Acid. $\text{SbAe}_3\text{O}, \text{HO}, 2\text{NO}_5$.—When the neutral nitrate is dissolved in dilute nitric acid, and the solution evaporated over the water-bath, the acid salt separates in oily drops, which solidify in a crystalline mass on cooling; and on dissolving this mass in water and evaporating, the acid salt is obtained in beautiful rhomboidal crystals, which dissolve readily in hot water. The salt thus obtained exhibits all the properties of the nitrate of stibethyl obtained by Löwig and Schweizer, in which they found 32.01 per cent. nitric acid; the above formula requires 31.67.

Acetate of Stibtriethyl.—When the solution of the oxide is saturated with acetic acid and the solution evaporated over the water-bath, there remains a thick syrupy residue, which does not crystallize, even after long standing in a warm place.

On the Stibamyls.*

By F. Berl  .

THESE compounds are formed by the action of iodide of amyl on antimonide of potassium. The latter substance (prepared by L  wig's process†) is finely pulverized, with addition of about half its bulk of dry sand; then introduced into glass flasks, in such quantity as to fill them to about two-thirds, and iodide of amyl added sufficient to moisten the mass throughout. After some time, and generally not till after the application of heat, a violent action takes place, attended with volatilization of the excess of iodide of amyl, which may be condensed by surmounting the flask with a distillation-tube. The flasks are then corked, their contents (a grey, pulverulent, coherent mass,) softened when cold with a small quantity of water, and emptied into a capacious cylinder, previously filled with carbonic acid gas. In this vessel, the product is repeatedly exhausted with ether; the ethereal solution, after it has become clear by standing, poured into a large flask filled with carbonic acid, and completely distilled off after addition of water or ether. The residue consists of *stibtriamyl*, protected from the action of the air by the water which is still present.

Pure *stibtriamyl* is a transparent, slightly yellowish liquid, very viscid below 20   C., more mobile at higher temperatures. Has a peculiar aromatic odour, and a bitter, somewhat metallic and very persistent taste. Sp. gr. = 1.1333 at 17   C. In contact with the air it fumes strongly, but does not take fire; it decomposes at the same time, with separation of a white powder. A drop of it placed on a piece of bibulous paper, and exposed to the air, becomes so strongly heated that the paper-fibre is charred. In presence of very small quantities (2 per cent) of amylic alcohol or iodide of amyl, *stibtriamyl* is also decomposed on exposure to the air, but without fuming or sensible rise of temperature. It is insoluble in water; sparingly soluble in absolute alcohol; very easily soluble in ether. Heated for eight days with iodide of amyl in a sealed glass tube, placed in the water-bath, it does not show any inclination to combine.

| <i>Stibtriamyl.</i> | | | | Calc. | Found. | | |
|--|---|---|-----|-------|--------|-------|-------|
| 30 C | . | . | 180 | 52.63 | 53.55 | 52.56 | 51.66 |
| 33 H | . | . | 33 | 9.65 | 10.00 | 10.00 | 10.00 |
| Sb | . | . | 129 | 37.72 | | | |
| <hr/> (C ₁₀ H ₁₁) ₃ Sb | | | | 342 | 100.00 | | |

* J. pr. Chem., lxx., 385; Ann. Ch. Pharm., xcvii., 316.

† Ann. Ch. Pharm., lxxv., 316.

If the stibtriamyl, prepared as above, is contaminated with free amylic alcohol (as when the iodide of amyl used in the preparation is impure) or with iodide of amyl, the following method may be adopted for the preparation of pure compounds. The impure stibtriamyl is dissolved in a mixture of ether and alcohol; bromine in alcoholic solution carefully added till its colour just begins to be permanent; then the bromide of stibtriamyl, precipitated by addition of a large quantity of water; the bromide converted into oxide of stibtriamyl, by means of silver-oxide suspended in alcohol; the resulting solution again precipitated by water; the separated oxide dissolved in hydrochloric acid and alcohol; and the pure chloride precipitated by another addition of water, and freed from a small quantity of water by continued heating to 100° , and the use of chloride of calcium.

Stibtriamyl combines with oxygen, iodine, &c., forming compounds, in which Berl   supposes 1 At. of the radical to be united with 2 At. of oxygen, &c.; the same view, in fact, as that proposed by L  wig for the compounds of stibethyl.*

Oxide of Stibtriamyl is produced by slow evaporation of an ethereal solution of stibtriamyl in contact with the air. There then remains a greyish yellow, very viscid, resinous mass, which becomes somewhat more fluid when heated, but readily decomposes at a higher temperature. Tastes and smells like stibtriamyl. Insoluble in water; sparingly soluble in hydrated alcohol and in ether; easily soluble in absolute alcohol. The alcoholic solution precipitates the oxides of the heavy metals from their salts. It dissolves readily in acids, and the resulting compounds are precipitated from their alcoholic solutions by water.

Chloride of Stibtriamyl.—Obtained by dissolving the oxide in hydrochloric acid, or by the method above described, is a yellowish, translucent liquid, viscid at ordinary, comparatively mobile at higher temperatures, heavier than water; dissolves in alcohol and ether. When precipitated from the alcoholic solution by water, it obstinately retains small portions of water and alcohol, from which it can only be freed by continued heating to 100° , and drying over chloride of calcium. Has a peculiar smell and taste, like the radical. Decomposes above 160° .

| | | Calc. | Found. | |
|------------------------------|-----|--------|--------|-------|
| Sb | 129 | 31.23 | | |
| 30 C | 180 | 43.69 | 44.59 | 43.63 |
| 33 H | 33 | 8.09 | 8.2 | 9.00 |
| 2 Cl | 70 | 16.99 | 16.83 | |
| <hr/> | | | | |
| $(C_{10}H_{11})_3Sb, Cl_2$. | 412 | 100.00 | | |

* Chem. Soc. Qu. J., v., 69. For another view of the constitution of the compounds of metalliodal radicals, containing 1 At. metal to 3 At. of an alcohol-radical, see page 278 of this volume.

Iodide of Stibtriamyl is obtained by dissolving the oxide in hydriodic acid and precipitating by water, or by adding iodine to the radical as long as it is discolored. Very much like the chloride. *Bromide of Stibtriamyl* is prepared in like manner, and exhibits similar properties.

| <i>Iodide.</i> | | | <i>Bromide.</i> | | |
|---|-------|--------|--|-------|--------|
| | Calc. | Found. | | Calc. | Found. |
| Sb . . . 129 | 21.65 | | Sb . . . 129 | 25.70 | |
| 30 C . . . 180 | 30.20 | 29.28 | 30 C . . . 180 | 35.86 | 36.04 |
| 33 H . . . 33 | 5.54 | 6.10 | 33 H . . . 33 | 6.57 | 6.75 |
| 2 I . . . 252 | 42.61 | 40.00 | 2 Br . . . 160 | 31.87 | 32.28 |
| <hr/> (C ₁₀ H ₁₁) ₃ Sb ₂ I ₂ . 594 100.00 | | | <hr/> (C ₁₀ H ₁₁) ₃ Sb ₂ Br ₂ . 502 100.00 | | |

When chloride or iodide of stibtriamyl is mixed with an alcoholic solution of nitrate of silver, as long as a precipitate forms, and then filtered, the filtrate forms an emulsion, from which, after standing for some time in a warm place, two liquids separate, the upper being light, yellow and mobile, and the lower a deep brown-red oil. The upper layer, when slowly evaporated, yields slender white crystals grouped in stars; they may be purified by recrystallization from dilute alcohol. The dark red oil likewise dissolves on addition of a large quantity of hydrated alcohol, and the solution, after standing for some time, yields the same crystals. These crystals melt at about 20°; the fused mass does not dissolve in alcohol so readily as the crystals. This salt, the only crystallizable compound of stibtriamyl, is the *Nitrate of Stibtriamyl*, (C₁₀H₁₁)₃Sb₂.2NO₆, (nitric acid by analysis 23.39 per cent.; by calculation 22.30); it is insoluble in water and ether, but dissolves in hydrated alcohol. Has a peculiar metallic taste.

By decomposing equivalent quantities of sulphate of silver and a haloid compound of stibtriamyl dissolved in alcohol, *Sulphate of Stibtriamyl* is obtained in solution. This salt was obtained only as an oily body, which yielded 18.03 per cent. sulphuric acid: the formula (C₁₀H₁₁)₃Sb₂SO₄ requires 18.26 per cent.

The white powder, formed by the action of the air upon stibtriamyl, is insoluble in ether, alcohol, and water; it does not dissolve in hydrochloric acid, but imperfectly in fuming nitric acid; slowly in aqua-regia. It remains unaltered even when strongly heated, not decomposing below a red heat. Berl  supposes it to be (C₁₀H₁₁)₃Sb₂SO₄ + 2SbO₃. When sulphuretted hydrogen was passed for some time through this compound suspended in alcohol, a white powder immediately separated, which gradually assumed an orange colour, and then formed a pulpy mass, which could not be filtered. After addition of a large quantity of alcohol and ether, the liquid, when left to stand in a warm place, deposited an orange-red, flocculent precipitate, which after drying formed a brownish yellow powder, insoluble in alcohol, ether, and water; this powder decomposed at a very high

temperature, and took fire when fuming nitric acid was poured upon it. Berl   regards this compound as $(C_{10}H_{11})_3SbS_2 + 2SbS_3$ (it gave 18.38 per cent. sulphur, the formula requiring 17.59). A compound, supposed to be identical with this, is formed by passing sulphuretted hydrogen for some time through an alcoholic solution of oxide of stibtriamyl.

When the product of the action of iodide of amyl upon iodide of potassium, instead of being exhausted with ether, was distilled in an atmosphere of carbonic acid, a liquid passed over, which was freed from undecomposed iodide of amyl by distillation over antimonide of potassium. The liquid thus obtained gave off when heated to $80^\circ C$. a colourless gas, which had a peculiar odour; burnt with a bright flame, diffusing a white smoke of antimonious oxide; was not absorbed by water; but when left for some time in contact with it, deposited a white coating of antimony on the sides of the vessel. After the gas had been driven off, the liquid was greenish yellow, had a peculiar aromatic odour and bitter taste; was tolerably mobile, and heavier than water. It was insoluble in water, but miscible in all proportions with alcohol and ether. Exposed to the air, it does not fume or become heated; when set on fire, it burns with a very bright flame, diffusing a white fume of antimonious oxide; when heated in pure oxygen gas, it explodes with the greatest violence; fuming nitric acid decomposes it with considerable evolution of heat. This compound is *Stibbiamyl*.

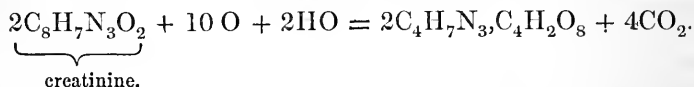
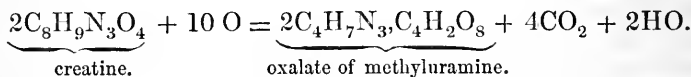
| | | Calc. | Found. | | | |
|--------------------------|-----|-------|--------|-------|--|-------|
| Sb . . . | 129 | 47.6 | | | | |
| 20 C . . . | 120 | 44.3 | 45.13 | 43.30 | | 44.83 |
| 22 H . . . | 22 | 8.1 | 8.80 | 9.01 | | 8.60 |
| <hr/> | | | | | | |
| $(C_{10}H_{11})_2Sb$. . | 271 | 100.0 | | | | |

When an ethereal solution of stibbiamyl is left to evaporate in the air, the resulting oxide absorbs carbonic acid. The radical, heated for some time to 100° in a stream of dry carbonic acid, yielded a liquid similar in properties to the pure radical, but more viscid. This liquid gave 42.19 per cent. carbon, and is regarded by Berl   as $(C_{10}H_{11})_2SbO, CO_2$, this formula requiring 41.52 per cent. C. The haloid salts of stibbiamyl are gummy liquids; the sulphate and nitrate are precipitated from their alcoholic solutions by water in the form of gummy masses, which dry up to amorphous solids.

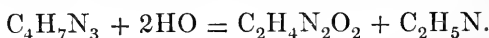
On Methyluramine and its Derivatives*.

By V. Dessaignes.

Two years ago, the author described† under the name *Methyluramine*, a strong base, produced by the action of mercuric oxide on creatine or creatinine.



This base may be regarded as a compound formed from urea and methylamine, with elimination of 2 At. water:



Creatine, on the other hand, may be regarded as glycolate of methyluramine *minus* water,—and sarcosine, its derivative, as an amide formed from glycolic acid and methylamine. If this view of the constitution of these bodies be correct, it must be possible to obtain methylamine from them. That such is the case, is shown by the following experiments.

The salts of methyluramine, heated with solution of potash, give off an abundance of alkaline vapours; and on absorbing these vapours by hydrochloric acid, evaporating the solution to dryness, and separating the greater part of the chloride of ammonium by means of absolute alcohol, an alcoholic solution is obtained, from which a salt crystallizes in shining laminæ; the platinum-salt prepared from this compound exhibits the composition of chloroplatinate of methylamine.

Creatine, heated with soda-lime, yields alkaline vapours, the platinum-salt of which, prepared as above, likewise exhibits the composition of chloroplatinate of methylamine.

Sarcosine, treated in the same manner, yields methylamine, which may also be obtained from it by the following reaction. When sulphate of sarcosine is dissolved in water, and heated with peroxide of lead, it is decomposed with brisk effervescence, the liquid assuming an alkaline reaction, and emitting a peculiar intoxicating odour: there is then formed a sulphate which may be decomposed by chloride of barium; and the resulting chloride, mixed with

* Compt. rend. xli, 1258; Ann. Ch. Pharm. xevii, 339.

† Compt. rend. xxxviii, 839.

bichloride of platinum, yields chloroplatinate of methylamine in small hexagonal tables very pure and having a strong lustre.

Lastly, creatine oxidized by nitric acid with the aid of heat, yields ammonia and a base which Chevreul noticed but did not analyze. This base is also methylamine; but the platinum-salt obtained from it is difficult to free from the accompanying sal-ammoniac.

Peroxide of lead oxidizes creatine on addition of sulphuric acid, and on heating the mixture, the acid becomes almost saturated. The sulphate thus formed was converted into a hydrochlorate, and from this a platinum-salt was prepared which crystallized in beautiful orange-coloured prisms, and exhibited the composition of chloroplatinate of methyluramine. The crystallized oxalate effloresces at 100°C ., and gives off 12.95 p.c. water; the base in the free state likewise exhibited all the properties of methyluramine; but the platinum-salt and the oxalate, even after repeated crystallizations, appeared to crystallize in forms different from those of the corresponding salts of methyluramine prepared with oxide of mercury.

When nitrous acid gas is passed through an aqueous solution of creatinine, the liquid effervesces, quickly turns brown, and then becomes turbid; and after a few hours, deposits an abundance of small indistinct and somewhat yellowish crystals, which become thick if left for some time in the liquid. These crystals are the nitrate of a new weak base, the salts of which are partially decomposed even by solution in water. A dilute solution of ammonia added to the acid liquid in sufficient quantity to saturate it, throws down a white amorphous powder insoluble in water. This base, after washing and drying, forms a light, coherent, friable mass, the powder of which is soft to the touch, and becomes electric by friction. It is tasteless. It dissolves in dilute acids when gently heated, and the solutions yield on cooling well crystallized and sparingly soluble salts.

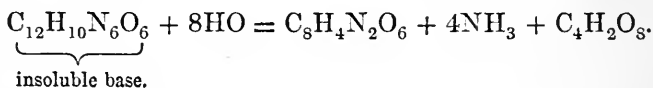
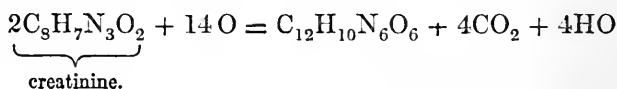
| <i>Free Base.</i> | | <i>Calc.</i> | <i>Found.</i> |
|--|----|--------------|---------------|
| 12 C | 72 | 33.64 | 34.46 |
| 10 H | 10 | 4.67 | 5.24 |
| 6 N | 84 | 39.29 | 38.14 |
| 6 O | 48 | 22.40 | 22.16 |
| <hr/> $\text{C}_{12}\text{H}_{10}\text{N}_6\text{O}_6$. . | | 100.00 | 100.00 |

The *hydrochlorate* forms short, deeply striated prisms, which give by analysis 25.18 p.c. C, 5.50 H, 27.40 N, and 17.95 Cl, agreeing nearly with the formula $2\text{C}_{12}\text{H}_{10}\text{N}_6\text{O}_6, 3\text{HCl} + 6\text{Aq}$. The *platinum-salt*, which is tolerably soluble, also forms large crystals, whose analysis gave 13.06 p.c. C, 2.83 H, 29.31 Cl, and 26.34 Pt, agreeing nearly with the formula $2\text{C}_{12}\text{H}_{10}\text{N}_6\text{O}_6, 3\text{HCl}$,

$3\text{PtCl}_2 + 6\text{Aq}$. The formulæ of these salts are somewhat unusual, and stand in need of further verification. The following reaction, however, appears to confirm the formula assigned to the base:

When the base is heated to 100°C . with excess of hydrochloric acid, it is readily decomposed, with formation of oxalic acid, sal-ammoniac, and a body which crystallizes in long shining prisms or laminae; dissolves slowly in cold, readily in hot water, and to a small amount in ether; has an unpleasant, almost metallic taste; is fusible; may be volatilized without decomposition; burns with flame and without residue; exerts a slight acid reaction upon litmus-paper, and does not precipitate the salts of lime, baryta, lead-oxide, cupric-oxide, zinc-oxide, or in dilute solution, chloride of mercury, or nitrate of silver. This body exhibits all the properties of the substance which Liebig* discovered as accompanying sarcosine in small quantity. To Liebig's description it is only necessary to add, that the substance precipitates nitrate of silver and mercurous nitrate in somewhat concentrated solutions. Its analysis gave 37.50 p.c. C, 3.12 H, and 21.87 N, agreeing very nearly with Liebig's formula $\text{C}_8\text{H}_4\text{N}_2\text{O}_6$.

The relations existing on the one hand, between creatinine and the insoluble base, and on the other hand between this base and the substance discovered by Liebig, may be expressed as follows:



Creatine acted upon by nitrous acid, yields a small quantity of a white powder, whose identity with the base just described was established by its yielding the substance $\text{C}_8\text{H}_4\text{N}_2\text{O}_6$ when heated to 100° with hydrochloric acid. The same substance was likewise obtained when the acid mother-liquor from which the nitrate of the new base had crystallized was left to evaporate over lime within a bell-jar.

* Ann. Ch. Pharm. lxii, 317.

THE
QUARTERLY JOURNAL
OF
THE CHEMICAL SOCIETY.

On the Reciprocal Precipitations of the Metals.

BY WILLIAM ODLING, M.B., L.R.C.P.,

SECRETARY TO THE CHEMICAL SOCIETY.

IN a paper read at the Cheltenham meeting of the British Association, I observed that "when metallic cadmium is introduced into an acidulated or non-acidulated solution of chloride of copper, with, or more slowly without, ebullition, the whole of the copper is deposited in a red pulverulent state; but that when a piece of clean copper foil is immersed in a boiling, moderately concentrated, and slightly acidulated solution of chloride of cadmium, after some little time, a very brilliant coating of cadmium, of a white or yellowish-white colour, is precipitated upon the copper." This last decomposition being in very curious antagonism to Bergmann's view of single elective affinity, I was induced to make some further experiments upon the reciprocal precipitations of the metals. The results I have obtained form the subject of my present communication to this society.

Silver and Mercury.—The introduction of metallic mercury into a solution of nitrate of silver is followed by a beautiful growth of crystalline silver, constituting the well-known *Arbor Lunæ*; but when a piece of clean silver foil is immersed in a solution of mercurous nitrate, the foil becomes eventually covered with a semiliquid layer of amalgam, is rendered very brittle throughout, and, when heated in a tube, affords an abundant mercurial sublimate. The same result was obtained with pure metallic silver,

reduced from the chloride by carbonate of soda. Acidification and continued ebullition of the solution, facilitate, but are not by any means essential to, the deposition of the mercury. Thus it appears that, under circumstances of the greatest similarity, mercury will precipitate silver, and silver will precipitate mercury, from their respective nitric solutions. Moreover, silver, when boiled in an acidified solution of corrosive sublimate, becomes covered with a layer of calomel and metallic mercury, but the result is not so striking as that with the mercurous salt.

Silver and Copper.—When metallic copper is introduced into a solution of nitrate or sulphate of silver, or into a liquid turbid from the suspension of chloride of silver, a precipitate of silver takes place almost immediately. The deposit is generally pulverulent, but may be obtained from the sulphate and chloride as a brilliant metallic coating, provided the dilution be very considerable. Ebullition facilitates the deposition of silver from dilute solutions, but interferes with the appearance of the coating. When on the contrary a piece of silver foil, or of pure silver reduced from the chloride, is boiled in an acidulated and strong solution of sulphate of copper, after some time, the silver acquires a faint coating of metallic copper. When viewed in certain positions, the red colour of the copper is very apparent. When, however, the cupric coating is so thin as to be imperceptible to the eye, the presence of the metal may be evidenced by moistening the foil with ammonia, whereby the deep blue-coloured solution of cupramide is gradually developed; or better still, by heating the foil, when the redness of copper or its suboxide is frequently brought out with such intensity as entirely to conceal the colour of the silver. With a solution of nitrate of copper, the silver becomes discoloured, but there is no decided metallic precipitate. With solution of chloride of copper the results are most decided. The silver foil, or reduced silver, becomes almost immediately covered, even in the cold, with an opaque layer of a pale dull copper colour. By continued ebullition the colour of the coating becomes much deeper and less red. The deposit is capable of receiving a polish. It does not dissolve in cold hydrochloric acid, dilute or concentrated, but simply becomes more bright and red coloured. By boiling the coated foil, however, for some time, in strong hydrochloric acid, the copper disappears with the evolution of gas, and the silver remains coated with chloride of silver, which a slight rubbing readily removes. On gently heating the coated foil, a fine bronze colour is developed. That the coating is really

metallic copper, and not the suboxide, to the colour of which it sometimes most approximates, is, I consider, unquestionable. Its insolubility in cold hydrochloric acid, and its solubility in the boiling acid with the evolution of gas, leave no doubt upon the subject. I have satisfied myself by a great number of experiments, that pure metallic copper is soluble to a very manifest extent in boiling hydrochloric acid. There is, indeed, no difficulty in collecting considerable quantities of hydrogen generated by the reaction of hydrochloric acid and copper. I have employed wire, foil, gauze, electrottype copper, and copper reduced from the chloride by zinc, always with the same result. Moreover, pieces of electrottype copper and thin foil, after a very protracted ebullition, disappear completely in the acid, and that without any absorption of oxygen from the air. Throughout the experiment, hydrogen continues to be liberated, the dissolved copper exists in the state of subchloride, and the liquid consequently remains colourless.

Antimony and Copper.—The precipitation of antimony upon copper was, I believe, originally pointed out by Reinsch as giving rise to a possible fallacy in the use of his process for the detection of arsenic, and the re-action is now well known to chemists; but I find that, when pure metallic antimony is boiled with an acidulated solution of chloride of copper, the antimony receives a thin, but obvious coating of copper. The deposition of copper upon antimony takes place also in the cold, though much less quickly. In this case, the presence of the copper may be readily evinced by means of ammonia.

Bismuth and Copper.—The reciprocal precipitations of these two metals resemble very closely those of antimony and copper. The precipitate of copper upon pure bismuth, however, is not so manifest to the eye as is the cupric deposit upon antimony, owing probably to the greater want of contrast in the colours of the metals.

Copper and Tin.—When an acidulated solution of chloride of copper is boiled with metallic tin, the whole of the copper is deposited in a red or black pulverulent state. I find, on the other hand, that when clean copper is boiled in a moderately strong and rather acid solution of stannous chloride, the tin is deposited upon the copper in the form of a brilliant metallic coating of a somewhat darker colour than either the arsenical or antimonial coatings. In operating with dilute tin solutions, from which under any circumstances it is difficult to obtain a deposit, I have not found a

large excess of acid advisable. Reinsch alludes to a tarnish being produced upon copper when boiled in tin solutions.

Copper and Lead.—The introduction of a piece of clean lead into a solution of chloride of copper is followed by a precipitation of metallic copper in a red or black pulverulent state. But I find, contrary to the usual statements on the subject, that copper immersed in a boiling, saturated, and strongly acidified solution of chloride of lead, acquires, after some few minutes ebullition, a beautiful metallic coating of a somewhat bluish colour. When the liquid is but slightly acidified, the deposit is very faint, and amounts only to a tarnish.

Copper and Cadmium.—These results have been already alluded to. For the precipitation of cadmium upon copper, especially when the solution is somewhat weak, the acidification must be very slight, or be dispensed with altogether. When the precipitation takes place slowly, the gradual concealment of the colour of the copper by the deposit of cadmium gives rise to some very beautiful chromatic appearances. An equivalent of cadmium will completely abstract the copper from a solution of the neutral chloride, containing very much more than an equivalent of copper. In one experiment, only 72·75 per cent. of an equivalent of cadmium precipitated an equivalent of copper. Of course a portion only of the precipitated copper was in the metallic state. I have not succeeded in obtaining a *decided* deposit of cadmium upon pulverulent copper precipitated by cadmium or zinc. Moreover, it is difficult to obtain a coating upon electrotype copper until the metal has been fused and hammered. When a plate of cadmium and a plate of copper are immersed in dilute acid, the electric current proceeds, as is well known, from the copper to the cadmium, and when the two metals are immersed in a boiling solution of chloride of cadmium, the current maintains the same direction. During the passage of the current, it seems that the cadmium is deposited electrolytically, and that no solution of the copper takes place.

Tin and Lead.—When clean lead is introduced into an acidified and moderately strong solution of stannous chloride, with or without ebullition, a deposition of metallic tin in the form of a powder, or of minute crystals, is produced. The decomposition is, however, very incomplete. On the other hand, when a piece of tin foil, or pure tin, is introduced into an acidified, boiling solution of chloride of lead, a deposit of lead speedily takes place. So uniform is the coating, and so well marked its colour, that the tin

actually appears to have been converted into lead foil. Fischer alludes to the precipitation of lead from the acetate by means of tin, but his reaction is much less marked than that with the chloride.

Tin and Cadmium.—The introduction of cadmium into an acidified solution of stannous chloride is followed by the formation of the well-known tin tree or *Arbor Jovis*. But when a piece of tin foil, or pure tin, is immersed in a solution of chloride of cadmium, the latter metal is deposited upon the tin as a film having a somewhat iridescent appearance. By boiling a piece of tin in a strong solution of chloride of cadmium, a very abundant deposit of cadmium may be obtained.

Tin and Iron.—A piece of clean iron or steel, immersed in a boiling and tolerably concentrated solution of stannous chloride, acquires after some little time a pulverulent coating of tin; but when a piece of tin foil, or pure tin, is boiled in an acidulated solution of ferrous chloride, the tin receives a black-coloured coating, and becomes extremely brittle throughout. After being well washed with water, and boiled with hydrochloric acid, it yields a solution in which the presence of iron is abundantly manifest. The brittle residue, moreover, exerts a slight effect upon a delicate magnet. The reciprocal actions of tin with nickel and cobalt respectively, resemble perfectly the above-mentioned reactions with iron.

Lead and Cadmium.—Lead is readily precipitated by cadmium. From a solution of acetate of lead the *Arbor Saturnii* is produced with nearly as much facility by cadmium as by zinc. But when clean lead, pure or commercial, is boiled in a moderately concentrated solution of cadmic chloride, it speedily receives a brilliant, uniform, yellowish-white coating of metallic cadmium.

Cadmium and Iron.—A piece of clean iron or steel, when boiled in a solution of cadmic chloride, acquires a complete coating of metallic cadmium, having exactly the same appearance as when precipitated upon copper or lead. On the other hand, cadmium foil boiled in a solution of ferrous chloride receives a black coloured coating. This coated foil acts slightly on the magnet, and when washed with water and boiled with hydrochloric acid, yields a solution in which the presence of iron is at once evidenced by the usual reagents. Nickel and cobalt respectively reciprocate with cadmium in a manner precisely similar to that of iron. I find also that iron is precipitated to a very great extent by zinc; but I have not been able to reverse the experiment and precipitate zinc upon iron. In estimating iron by means of a standard solu-

tion of permanganate of potash, zinc is occasionally added to the iron solution, for the purpose of reducing the ferric to the ferrous salt. Unless care be taken to boil the liquid for some time with hydrochloric acid after the disappearance of the zinc, a very serious error may be introduced into the process by the abstraction of iron from the liquid.

From the above described experiments it appears that the reciprocal precipitation of the metals is a phenomenon of considerable generality; how, then, are the apparently antagonistic results to be explained? There can, I conceive, be no doubt whatever that, under certain specified conditions, the tendencies to the formation of some one particular compound are greater than the tendencies to the formation of some other analogous compound. Thus at a red heat, the tendencies to the formation of protoxide of lead are greater than the tendencies to the formation of the analogous protoxide of silver. Disregarding its etymology, we make use of the word affinity to express the tendencies which lead and oxygen have to unite with each other.* Admitting then to the full, that there are stronger tendencies or affinities leading to the production of one compound AB, than of another AC, we have to inquire how it is that AC is sometimes produced to the prejudice of AB.

From a variation in the conditions of the experiment.—It seems that the affinities leading to the production of any compound are not absolute, but variable, according to circumstances. Thus, at a red heat the tendencies to the production of oxide of iron or oxide of lead are greater than at ordinary temperatures. Now it is not improbable that the affinity of A for B shall in one set of conditions be greater than, and in another set of conditions be less than, that of A for C. But irrespective of any absolute variation in the powers of the different affinities, an alteration in the condition of the experiment brings other forces into play. Thus the well-known results of passing hydrogen over red-hot oxide of iron, and steam over red-hot metallic iron, have received an explanation from Mr. Graham to the effect—that in the

* In such a simple case as the above, the expressions affinity and chemical attraction are perfectly admissible. But when applied to more complex instances of combination, the phraseology becomes objectionable as necessarily representing to our minds some one or other speculative view concerning the constitution of the body under consideration. Thus in sulphate of barium, Ba^2SO^4 , are we to speak of the affinity of baryta, Ba^2O , for sulphuric anhydride SO^3 ; or that of barium, Ba^2 , for oxysulphide, SO^4 ; or that of peroxide of barium, Ba^2O^2 , for sulphurous anhydride, SO^2 ; &c., &c. It is in this point of view that I take exception to the word affinity, which, however, it is scarcely possible to avoid employing.

former case, the diffusive tendency of steam into an atmosphere of hydrogen determines the reduction, and in the other, the diffusive tendency of hydrogen into an atmosphere of steam determines the oxidation of the iron. In a similar manner, when copper is boiled in a strong solution of chloride of cadmium, the diffusive or solvent force of chloride of copper may determine its formation. Water saturated with chloride of cadmium would be greedy of chloride of copper, and would yield the former metal in willing exchange for the latter. The solvent power of the cadmic solution for the cupric salt would exert a disposing affinity.

From the effect of mass.—The amount of evidence in favour of the general proposition by Berthollet, that “la quantité peut suppléer à la force de l’affinité pour produire un même degré de saturation,” is now so great, as to render it almost indisputable. It is highly probable indeed that, were it not for interfering circumstances, if we had the electro-negative body A, and the metals B and C in excess, A would divide itself in the ratio of

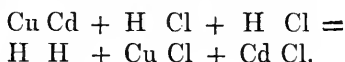
$\frac{x b}{x b + y c}$ to $\frac{y c}{x b + y c}$, where the tendency to form $AB = b$,

the tendency to form $AC = c$, the amount of $B = x$, and the amount of $C = y$. It is obvious, however, that in many cases, superficies rather than mass will most influence the result. Mass may possibly exert a considerable effect in the cases where the precipitation of a metal from its acid solution is accompanied by a liberation of hydrogen. It is not improbable that the nascent hydrogen may preferably reduce the metal which was originally dissolved, in consequence of the greater quantity of the original, than of the subsequently formed salt. I find also that when a piece of clean iron is boiled in a solution of cadmic chloride containing a little cupric chloride as an impurity, copper and cadmium are simultaneously precipitated upon the iron which thus becomes coated with a species of brass. The precipitation of cadmium, however, despite its superior affinity, takes place to a very much greater extent than does the precipitation of copper, in consequence, I believe, of its superior mass. With a strong solution of cadmium the whole of the copper is not precipitated by iron, even after a somewhat protracted ebullition. Copper may, however, be readily removed from a dilute solution of cadmium, by agitating it with clean iron in the cold.

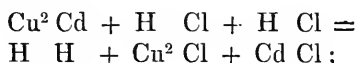
As a result of double decomposition from homogeneous affinity.—The propriety of representing chlorine, hydrogen, and the metals,

as binary molecules Cl Cl, H H, M M, respectively, as advocated by Brodie, Laurent, Gerhardt, and others, appears to receive confirmation from the phenomena of the mutual precipitation of the metals. By considering the precipitation of one metal upon another as an instance, not of single, but of double decomposition, I was enabled to explain several of the results I have already described. But, curiously enough, I find, not only that my explanation has been in its general nature anticipated by Berthollet, but that our modern notion of the homogeneous affinity of Cu for Cu, Hg for Hg, &c., is described by the same author in unmistakeable language. In accordance with these views, the precipitation of cadmium upon copper may be represented by the equation $\text{Cu Cu} + \text{Cd Cl} = \text{Cu Cd} + \text{Cu Cl}$, and the decomposition be determined by the circumstance that, in the conditions of the experiment, the sum of the affinities of Cu for Cd, and of Cu for Cl exceeds that of the affinities of Cu for Cu and Cd for Cl. Is there, however, any proof that a cadmide of copper is really formed? We know that an alloy differs greatly from a mixture of two metals, in the phenomena of its solution in acids. Thus an alloy of silver and platinum dissolves in nitric acid; but with the two metals in contact or mixture, there is an electric current generated; the silver is dissolved, and the platinum is left. An alloy of zinc and copper dissolves in hydrochloric acid; but with the two metals in contact or mixture, there is an electric current generated; the zinc is dissolved, and the copper remains. The solubility of pure copper in hydrochloric acid, to which I have before adverted, is not opposed to this result. Iron by itself is readily soluble in hydrochloric acid, but is not so in the presence of zinc. Now I find that a piece of copper coated with cadmium, and a coil of copper and cadmium foils rolled up together, behave very differently when treated with hydrochloric acid. Hydrochloric acid of the ordinary strength was diluted with a third of its volume of water and two equal portions boiled. Into one of the boiling liquids was immersed the compound coil, and into the other the coated foil. In both cases there was a considerable evolution of hydrogen, greater, however, with the coil than with the foil. The liquid in which the coil was immersed remained perfectly colourless, and even after a lapse of several hours had not dissolved a trace of copper. The liquid in which the coated foil was immersed became immediately green, and long before the cadmium had disappeared, contained copper in very considerable quantities, thus proving that the metallic deposit

partook of the characters of an alloy. In this case the solution probably took place according to the equation



It might possibly have been



but I am inclined to think from the instantaneous development of the green colour, in circumstances where an absorption of oxygen would have been difficult, that the former equation is correct. If the precipitation of one metal upon another be really due in great measure, as I believe it to be, to the affinity of the one metal for the other, the general result that I have arrived at, namely, that if the metal A can precipitate the metal B, the metal B will also precipitate the metal A, is sufficiently accounted for. This reciprocity, of course, will not be manifested when the tendency to form the salt of the one metal is very much greater than the tendency to form the salt of the other metal.

Note on the purity of the metals employed in the above-described experiments.

The pure silver was reduced from chloride of silver by fusion with carbonate of soda. The pure copper was precipitated electrolytically, upon a copper surface, by the current of a Daniell's cell. To obtain pure bismuth, nitrate of bismuth, after several crystallizations, was ignited, and the heated oxide reduced in a bulb-tube by a current of hydrogen gas. The hydrogen, prepared from the reaction of zinc and sulphuric acid, was passed successively through a solution of nitrate of silver, through a solution of hydrate of potash, and through oil of vitriol. 33·230 grains of oxide of bismuth, lost 3·445 grains. This result corresponds very closely with that obtained by Gmelin:—

| | | Calculated. | Lagerhjelm. | Gmelin. | Odling. |
|----|---------|-------------|-------------|---------|---------|
| Bi | . . 213 | 89·87 | 89·863 | 89·67 | 89·64 |
| O | . . 24 | 10·13 | 10·137 | 10·33 | 10·36 |

The pure lead was obtained from re-crystallized nitrate of lead. The salt was ignited and fused before the blowpipe with carbonate of soda. The pure tin was obtained electrolytically by immersing a bar of tin into two strata of liquid, the lower being a solution of crystallized stannous chloride, the upper being acidulated water. The pure antimony was obtained by incinerating re-crystallized tartar-emetic with carbonate of soda. The cadmium foil came into my hands as such. In its solution I was unable to detect the presence of zinc, or, with the exception of a very minute trace of iron, any other metal. The iron was employed only in the forms of commercial rolled iron and hard steel.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

November 3, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

“The Pharmaceutical Journal:” from the Editor.

“The American Journal of Science:” from the Editors.

“The Journal of the Franklin Institute:” from the Institute.

“The Canadian Journal of Industry and Science:” from the Editor.

“The Proceedings of the Royal Society:” from the Society.

“The Transactions and Proceedings of the Royal Society of Edinburgh:” from the Society.

“Memoirs of the Manchester Philosophical Society:” from the Society.

“Notes of Meetings and List of Members of the Royal Institution:” from the Institution.

“On Food, by Dr. Marcet:” from the Author.

Richard V. Tuson, Esq., of St. Bartholomew's Hospital, was elected a Fellow of the Society.

The following papers were read:—

“On the Reciprocal Precipitations of the Metals:” by W. Odling, M.B.

“On a new Series of Organo-thionic Acids:” by John T. Hobson.

November 17, 1856.

Dr. WILLIAMSON, Vice-President, in the Chair.

The following donations were announced :—

“Proceedings of the Liverpool Literary and Philosophical Society :” from the Society.

“The Journal of the Franklin Institute :” from the Institute.

“The Journal of the Society of Arts :” from the Society.

The following papers were read :—

“On a new Volumetric Method for the determination of Copper :” by E. O. Brown.

“On the Action of Light upon Chloride of Silver :” by Frederick Guthrie, B.A., Ph.D.

December 1, 1856.

Dr. WILLIAMSON, Vice-President, in the Chair.

The following donations were announced :—

“The American Journal of Science :” from the Editors.

“The Journal of the Society of Arts :” from the Society.

“The Journal of the Franklin Institute :” from the Institute.

“The Pharmaceutical Journal :” from the Editor.

William Baker, Esq., Lead Works, Sheffield, was elected a Fellow of the Society.

The following papers were read :—

“On Compounds obtained by the action of Anhydrous Sulphuric Acid on the Chlorides of Hydrogen, Ethyl, and Methyl :” by R. Williamson.

“Note on the Action of Bichloride of Carbon on Ethylate of Potash :” by F. B. Lockwood.

“On some Thermo-electrical Properties of the metals Bismuth and Antimony, when used as single elements :” by Richard Adie.

December 15, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following gentlemen were elected Fellows of the Society :—

William Wallace, Esq., Andersonian Institution, Glasgow.

W. H. Perkin, Esq., Royal College of Chemistry.

John Horsley, Esq., Cheltenham.

John Hodgson Jones, Esq., 1, Poets' Corner, Westminster.

Charles Lowe, Esq., Halifax.

The following papers were read :

“On the Saponification of Resin:” by A. G. Anderson.

“On a Compound obtained by the action of fuming Sulphuric Acid on Chloride of Phenyl:” by L. Hutchings.

TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1856.

A.

- Absorption.—Absorptiometric researches: by *L. Carius*. Ann. Ch. Phys. [3] xlvii. 418.
- Law of absorption for ammoniacal gas: by *L. Carius*. Ann. Ch. Pharm. xcix. 129.
- Acetal.—Researches on acetal and on the glycols: by *A. Wurtz*. Compt. rend. xliii. 478; Ann. Ch. Phys. [3] xlviii. 370; Ann. Ch. Pharm. c. 110.
- Acetates.—On crystallised acetate of magnesia: by *C. v. Hauer*. J. pr. Chem. lxvi. 248; Chem. Gaz. 1856, 61.
- Action of chloride of sulphur on acetate of soda: by *W. Heintz*. Pogg. Ann. xcvi. 458.
- Acetylamine.—On acetylamine: by *J. Natanson*. Ann. Ch. Pharm. xcvi. 291; Ann. Ch. Phys. [3] xlviii. 111; Chem. Gaz. 1856, 303.
- Acid, Acetic.—On the acidimetry of acetic acid: by *E. C. Nicholson* and *D. S. Price*. Chem. Gaz. 1856, 30.
- Acid, Alloxanic.—On alloxanic acid: by *G. Städeler*. Ann. Ch. Pharm. xcvi. 120; Chem. Gaz. 1856, 73.
- Acid, Anilotic.—On anilotic acid: by *R. Piria*. Ann. Ch. Pharm. xcvi. 253; Chem. Gaz. 1856, 169.
- Acid, Amylophosphoric.—See *Amyl*.
- Acid, Anisoic.—On anisoic acid: by *H. Limpricht*. Ann. Ch. Pharm. xcvi. 364; Chem. Soc. Qu. J. ix. 186; Ann. Ch. Phys. [3] xlviii. 117; Chem. Gaz. 1856, 167.
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- Acid, Arsenic.—See *Arsenic*.
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2002

THE
QUARTERLY JOURNAL
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I.—*On some Points in the Composition of Wheat-Grain, its Products in the Mill, and Bread.*

BY J. B. LAWES, F.R.S., F.C.S., AND
J. H. GILBERT, PH. D., F.C.S.

THE composition of the grain yielding the most important article of human food in temperate climates, its yield of valuable products, and the varying composition either of the grain itself, or of these products, according to the conditions of growth, or the circumstances of after preparation, are subjects worthy the attention equally of states and of men of science. Accordingly we find, that a chemical examination of wheat-grain and its products, has from time to time been undertaken by chemists of repute; sometimes as a matter of private investigation, and at others of public inquiry; and almost as numerous as the names of the experimenters, are the special lines of research which they have selected.

We are indebted to Beccaria for the first notice, more than a century ago, of the gluten in wheat. Among the earlier investigators of the subsequent period, are, Proust, Vauquelin, De Saussure and Vogel, who have examined the proximate principles, and some of the changes to which they are subject, in various descriptions of wheat, of flour, or of bread. M. Bous-singault has somewhat elaborately studied various branches of the subject more recently; and we are indebted to Dumas,

Payen, Johnston, and Dr. R. D. Thomson for original, as well as a considerable amount of collected information. The most recent, on some points the most detailed, and from advance in methods, perhaps on some also the most reliable, are the results of M. Peligot in 1849, on the proximate constitution of various kinds of wheat, and of M. Millon in 1849 and 1854, on somewhat similar points. Lastly, in 1853 M. Poggiale, and in 1855 Dr. MacLagan, have given the results of their investigations on the characters and composition of bread.

Besides these more general investigations, we have had in recent times many special inquiries connected with our subject. Thus, M. Boussingault has given us analyses of the ashes of wheat; and many other such analyses have been made in Germany, and elsewhere, since the first appearance, in 1840, of Baron Liebig's work on "Chemistry in its Applications to Agriculture and Physiology." In this country, Mr. Way has given us the most extensive series of wheat-grain-ash analyses, his list including those of 26 specimens or descriptions.

The plan of our own investigation, which unfortunately has been much less perfectly filled up than we at first intended, was entered upon more than a dozen years ago, and was devised with reference to the following points:—

1st. The influence of varying characters of season, and of various manuring, upon the organic and mineral composition of wheat grain.

2ndly. The characters of varieties, especially in relation to their adaptation, and the qualities they then develop, under the influence of broader distinctions as to locality, altitude, latitude, and varying climatic circumstances generally.

It is in the second branch of the inquiry that we have fallen the furthest short of our intentions. With a view to its prosecution, a journey through the chief corn growing districts of Europe, commencing at the northernmost point at which wheat is grown successfully, was about to be undertaken in 1848; but the social disturbances on the continent at that period, necessarily prevented it. The plan proposed was—to collect information, as to the geological and meteorological characters of the various localities, as to the mode of culture, and as to the general acreage yield, both in straw and grain; and lastly, to procure characteristic specimens for chemical examination at home. Failing entirely in the execution of this design, the Exhibition of 1851 was looked forward to as an oppor-

tunity for procuring specimens not only of wheat, but of other vegetable products, and perhaps also important particulars of their growth, from various countries and climates. Such, however, was the division of authority, and such the alleged preference given to public institutions in such matters, that, whether the latter benefited or not, the collection which we, as private individuals, were enabled to make, was entirely inadequate to our object. From these difficulties it is, that our second main object of inquiry was necessarily to a great extent abandoned; and chiefly for this reason, but partly owing to the pressure of other subjects; the first or more limited or local branch of the investigation has in recent years been but imperfectly followed up. And, as it is probable that it must for some time remain so, it has been thought desirable thus to put on record the results already obtained; hoping that they may serve the double purpose, of confirming or adding to previously existing knowledge, and of indicating to others the points most requiring further study.

The following is a brief outline of the plan of investigation which has yielded the results which we have now to lay before the Society.

From the season 1843-4, up to the present time, wheat has been growing in the same field continuously, both without manure, by ordinary, and by various chemical manures. As a general rule, the same description of manure has succeeded year after year on the same plot of land. The amount of produce, corn, straw, and chaff, and its characters as to weight per bushel, &c., have in every case, been carefully ascertained and recorded. Samples from each plot—both grain and straw—have also been collected every year. Of each of these samples two weighed portions are coarsely ground; the *dry matter* determined at a temperature of 212° ; and the *ash* by burning on sheets of platinum, in cast iron muffles arranged for that purpose.* Other weighed portions of grain and straw are partially dried, so as to prevent their decomposition; and in this state they are preserved for any examination of their organic constituents. By this course of procedure, a vast mass of results has been obtained, illustrating the influence of season and manuring, upon the percentage of dry substance, and of mineral constituents, in the produce. In selected cases, the *nitrogen* in the grain, and in the straw, has been determined.

* The dry matter and ash, were not determined in such complete series in the earlier years, as in the later.

A summary table of these dry matter, ash, and nitrogen results, will be given below. In from twenty to thirty cases complete analyses of the grain-ashes have been made, and the results of these will be given in full.

Besides the experiments above described, in selected cases, chiefly from the produce of the earlier years of the field experiments, it was sought to ascertain the comparative *yield of flour*, and also the characters of the flour, of grain grown by different manures in the same season, or by the produce of different seasons. The *colonist's steel handmill* was first had recourse to for this purpose. But it was soon found, that it was extremely difficult so to regulate the machine, as to secure uniform action upon the different grains; and it was further found, that the grain, and especially the bran, was cut up rather than crushed, so as to leave too much of flour in the portion separated as bran, and too much of bran in that separated as flour; and hence the results were not sufficiently comparable with those of the ordinary mill. Arrangements were therefore made for prosecuting the inquiry at a flour mill in the neighbourhood, worked by water power. Weighed quantities of the selected samples (from 125 to 250 lbs. each), were passed through the stones, and the "*meal*" thus obtained, through the dressing machine, under our own personal superintendence; great care being taken to clear from the different parts of the apparatus the whole of one lot, before another was commenced upon.

The yield in the dressing machine of each of the different products was ascertained, and its percentage in relation to the total grain or its "*meal*," has been calculated. Portions of each of these products have had their dry matter (at 212°), and their mineral matter (by burning on platinum), determined. The percentage of nitrogen in a few selected series—from the finest flour down to the coarsest bran—has also been estimated; and in the same cases, the amounts of one or two of the more important constituents of the ash have also been determined. The results of these dry matter, ash, nitrogen, and constituent of ash determinations, in the series of different products obtained in the mill, will be given in tables further on.

The original design, was to complete the examination of the mill products, by determining in several series of them, the percentage of each of their proximate organic principles; and also the amount and composition of mineral matters, associated with

them respectively. It was hoped, by this latter inquiry, to obtain important collateral information, bearing upon the influence of various constituents upon the healthy and special development of the plant. Although, however, specimens of the flour are preserved for this purpose, as well as the ashes of each crude product, it is feared that this subject cannot be proceeded with, at least for a considerable time to come.

Portions of the different products of the dressing machine (including more or less of the finest flour, of the more granular, or of the more branny particles respectively), from grains of somewhat various history of growth, have been experimented upon to ascertain their comparative bread-making qualities; and these results, together with a few examinations of baker's bread, and a discussion of the results of other experimenters, as to the yield of bread from a given amount of flour, and the percentage of water and of nitrogen in the former, will be given below.

With this short outline of the plan of investigation which has been pursued, we proceed now to a discussion of the results which have been obtained.

In Table I. are given, in the first four columns, certain prominent characters of the produce of each of ten years of the successive growth of wheat as above described. The items are:—

The total produce per acre (corn and straw), in lbs.;

The per cent. of corn in the total produce;

The per cent. of dressed corn in the total corn; and,

The weight per bushel of dressed corn in lbs.

The figure given for each year, generally represents the average of about 40 cases; and the characters enumerated are the best which can be given in a summary and numerical form, to indicate the more or less favourable condition of the respective seasons for the healthy development of the crop, and the perfect maturation of the grain.

In the second set of three columns are given, side by side with the general characters just described, the percentages in the grain of each year—

Of dry substance;

Of ash in dry substance; and,

Of nitrogen in dry substance;

the two former items being in most cases the average of 30 to 40 cases in each year; but the per cent. of *nitrogen*, is in each instance, the mean of a few selected cases only.

In the third set of three columns, are given similar particulars relating to the composition of the straw. The percentages of dry substance and of ash in the straw, are however not the averages of so many cases in each year, as are those for the corn; and the determinations of nitrogen in the straw, have also been made in fewer cases than in the grain.

It will thus be seen, that the table affords a summary view of a really enormous amount of experimental result, and we ought to be able by its means to discover, at least the broad and characteristic effects of varying seasons, upon the composition of the crop.* This indeed is all we could hope to attain, in such a mere outline and general treatment of the subject as is appropriate to our present purpose.

TABLE I.
GENERAL SUMMARY.

| Harvests | Particulars of the Produce. | | | | Composition of GRAIN. | | | Composition of STRAW. | | |
|----------|---------------------------------------|----------------------------------|---------------------------------------|---|-----------------------|-----------------------|----------------------------|-----------------------|-----------------------|----------------------------|
| | Total corn and straw per acre in lbs. | Per cent. corn in total produce. | Per cent. dressed corn in total corn. | Weight per bushel of dressed corn in lbs. | Per cent. dry (212°.) | Per cent. ash in dry. | Per cent. nitrogen in dry. | Per cent. dry (212°.) | Per cent. ash in dry. | Per cent. nitrogen in dry. |
| 1845 | 5545 | 33·1 | 90·1 | 56·7 | 80·8 | 1·91 | 2·25 | .. | 7·06 | 0·92 |
| 1846 | 4114 | 43·1 | 93·2 | 63·1 | 84·3 | 1·96 | 2·15 | .. | 6·02 | 0·67 |
| 1847 | 5221 | 36·4 | 93·6 | 62·0 | .. | .. | 2·30 | .. | 5·56 | 0·73 |
| 1848 | 4517 | 36·7 | 89·0 | 58·5 | 80·3 | 2·02 | 2·39 | .. | 7·24 | 0·78 |
| 1849 | 5321 | 40·9 | 95·5 | 63·5 | 83·1 | 1·84 | 1·94 | 82·6 | 6·17 | 0·82 |
| 1850 | 5496 | 33·6 | 94·3 | 60·9 | 84·4 | 1·99 | 2·15 | 84·4 | 5·88 | 0·87 |
| 1851 | 5279 | 38·2 | 92·1 | 62·6 | 84·2 | 1·89 | 1·98 | 84·7 | 5·88 | 0·78 |
| 1852 | 4299 | 31·6 | 92·1 | 56·7 | 83·2 | 2·00 | 2·38 | 82·6 | 6·53 | 0·79 |
| 1853 | 3932 | 25·1 | 85·9 | 50·2 | 80·8 | 2·24 | 2·35 | 81·0 | 6·27 | 1·20 |
| 1854 | 6803 | 35·8 | 95·6 | 61·4 | 84·9 | 1·93 | 2·14 | 83·7 | 5·08 | 0·69 |
| Means | 5053 | 35·4 | 92·1 | 59·6 | 82·9 | 1·98 | 2·20 | 83·2 | 6·17 | 0·82 |

Leaving then out of view all minor points, and confining ourselves to our already defined object—namely, that of ascertaining the general direction of the influence of variation of season upon the composition of the wheat crop—we cannot fail to see, that wherever the three items indicating the *quality* of the produce

* It should be stated, that up to 1848 inclusive, the description of wheat was the Old Red Lammas; from 1849 to 1852 inclusive, it was the Red Cluster, and since that time the Rostock. The variations, according to season, both in the characters and composition of the produce, are, however, very marked within the period of growth of each separate development.

markedly distinguish the crop as favourably developed, we have a general tendency to a high percentage of dry substance, and to a low percentage both of mineral matter, and of nitrogen, in that dry substance. This generalization is more especially applicable to the grain; but with some exceptions, mostly explicable on a detailed consideration of the circumstances and degree of its development, it applies to a great extent to the straw also.

Let us take in illustration the extreme cases in the table. The seasons of 1846, 1849, and 1851, with in the cases of the two latter large produce also, give us the best proportion of corn in total produce, more than the average proportion of dressed corn in total corn, and the highest weight per bushel—a very significant character. With this cumulative evidence as to the relatively favourable development and maturation of these crops, we find the grain in two of the cases, to be among the highest in percentage of dry matter; and in the third (1849), though not so high as we should have expected, it is still above the average. The percentages of mineral matter and of nitrogen in the dry substance of the grain, are at the same time, in these three cases, the lowest in the series. The seasons of 1850 and 1854 again, with large amounts of produce, yielded also very fairly developed grain; and coincidently they afford a high percentage of dry substance, and lower percentages both of mineral matter, and of nitrogen, in that dry substance, than the cases of obviously inferior maturation. With some exceptions, it will be seen, that the straws also of these 5 better years, give a tendency to low percentages both of mineral matter and of nitrogen in their dry substance.

Turning now to the converse aspect, the season of 1853, shows itself in the general characters of the produce, to have been in every respect the least favourable to the crop; and it should be added that in this instance (as well as in 1845 to which we shall next refer), the seed was not sown until the spring. In 1853 the produce of grain was small as well as very bad in quality; and with these characters, we have in the grain nearly the lowest percentage of dry matter, and the highest percentage of ash and of nitrogen in that dry matter. In the straw, too, the dry matter is low, the ash somewhat high, and the nitrogen much the highest in the series. In 1845, another year of spring-sowing, and at the same time of very bad quality of produce, we have nevertheless a large *amount* of growth; a fact which tends to explain some of the differences in composition as compared with 1853. Thus, 1845

gives us low percentage of dry matter, but not very high, either ash or nitrogen, in the grain. The straw, however, gives high percentages both of ash and of nitrogen; it being in the latter point next in order to 1853. The seasons of 1848 and 1852 again show low characters of produce. The former has coincidently the lowest percentage of dry matter in the grain in the series; and both have high percentage of ash and nitrogen in the dry substance of the grain. In the straw, the ash is in 1848 the highest, and in 1852 above the average; the nitrogen in dry matter of straw being however in neither instance high.

In several of the cases here cited, there are deviations from our general assumption on one point or other. But an examination in greater detail, would in most or all of them clear up the apparent discrepancy. When indeed, we bear in mind how infinitely varied was the mutual adaptation of climatic circumstances to stage of growth of the plant, in almost every case, it would indeed be anomalous, did we not find a corresponding variation on some point or other, in the characters or composition of the crop. Still, we have the fact broadly marked, that within the range of our own locality and climate, high maturation of the wheat crop is, other things being equal, generally associated with a high percentage of dry substance, and a low percentage of both mineral and nitrogenous constituents. Were we, however, extending the period of our review, and going into detail as to varying climatic circumstances, interesting exceptions could be pointed out.

It may be observed in passing, that owing to the general relationships of the amounts of corn to straw, and the generally coincident variations in the percentages of nitrogen in each, the tendency of all these variations is in a degree so to neutralize each other, as to give a comparatively limited range of difference in the figures, representing for each year, the percentage of nitrogen in the dry substance of the total produce—corn and straw together.

The tendency of maturation, to reduce the percentages of mineral matter, and frequently of nitrogen also, is not observable in corn crops alone. We have fully illustrated it in the case of the turnip; and our unpublished evidence in regard to some other crops, goes in the same direction. The fact is indeed very important to bear in mind; for it constitutes an important item in our study of the variations which are found to exist in the composition both of the organic substance, and of the ash, of one and the same crop, grown under different circumstances. We may particularly observe,

that the obvious reduction in the percentage of nitrogen in wheat-grain, the more, within certain climatic limits, the seed is perfected, is in itself a fact of the highest interest; and it is the more so, when we consider how exceedingly dependent for full growth, is this crop upon a liberal supply of available nitrogen within the soil.

Bearing in mind, then, the general points of relationship which have been established between the characters of the crop as to development and maturation on the one hand, and the percentage amounts of certain constituents on the other, let us now see—what is the general influence of characteristic constituents of *manure*, upon the characters and composition of our wheat crop, which is allowed to remain on the land until the plant has fulfilled its highest function—namely, that of producing a ripened seed?

In illustration of this point we have arranged in Table III, the same particulars as to general character of the crop, and as to the composition of the produce, from several individual plots during the ten years; instead of the average of the series in each year, as in Table I. The cases selected for the comparison are:—

1. A continuously unmanured plot;
2. A plot having an excess of ammoniacal salts alone every year;
3. The average of several plots, each having the same amount of ammoniacal salts as the plot just mentioned, but with it, a more or less perfect provision by manure, of the *mineral constituents* also.

It would be impossible to give the detail supplying all the results collected in this Table III; but perhaps it is only proper that we should do so, so far at least as the percentage of nitrogen in the dry substance of the grain is concerned.

TABLE II.

Determinations of Nitrogen per Cent. in the Dry Matter of
Wheat Grain grown at Rothamsted.

| Harvests | | | EXPERIMENTS. | | | | | Mean. |
|--|----|----|--------------|------|------|------|------|-------|
| | | | 1 | 2 | 3 | 4 | 5 | |
| Unmanured. | | | | | | | | |
| 1845 | .. | .. | 2.28 | 2.21 | 2.33 | 2.30 | .. | 2.28 |
| 1846 | .. | .. | 2.11 | 2.12 | .. | .. | .. | 2.11 |
| 1847 | .. | .. | 2.11 | 2.08 | 2.22 | 2.22 | .. | 2.16 |
| 1848 | .. | .. | 2.33 | 2.34 | 2.32 | 2.37 | .. | 2.34 |
| 1849 | .. | .. | 1.85 | 1.83 | 1.91 | .. | .. | 1.86 |
| 1850 | .. | .. | 2.07 | .. | 2.10 | 2.07 | .. | 2.08 |
| 1851 | .. | .. | 1.80 | 1.74 | 1.89 | 1.76 | .. | 1.80 |
| 1852 | .. | .. | 2.31 | 2.23 | 2.33 | 2.31 | .. | 2.31 |
| 1853 | .. | .. | 2.26 | .. | 2.33 | 2.38 | .. | 2.32 |
| 1854 | .. | .. | 2.06 | 2.06 | 1.98 | 1.96 | .. | 2.01 |
| Manured with Ammoniacal Salts only. | | | | | | | | |
| 1845 | .. | .. | 2.18 | 2.29 | 2.22 | 2.23 | .. | 2.23 |
| 1846 | .. | .. | 2.18 | 2.12 | 2.29 | 2.19 | .. | 2.19 |
| 1847 | .. | .. | 2.35 | 2.29 | 2.42 | 2.32 | .. | 2.34 |
| 1848 | .. | .. | 2.39 | 2.41 | 2.39 | 2.49 | .. | 2.42 |
| 1849 | .. | .. | 1.89 | .. | 2.04 | 1.92 | .. | 1.95 |
| 1850 | .. | .. | 2.13 | .. | 2.08 | 2.19 | .. | 2.13 |
| 1851 | .. | .. | 2.15 | 2.12 | 2.09 | 2.25 | .. | 2.15 |
| 1852 | .. | .. | 2.41 | 2.50 | 2.44 | 2.58 | .. | 2.48 |
| 1853 | .. | .. | 2.43 | 2.48 | 2.37 | 2.44 | .. | 2.43 |
| 1854 | .. | .. | 2.31 | 2.22 | 2.31 | 2.37 | .. | 2.30 |
| Manured with Ammoniacal Salts and Mineral Manure. (Mixed Plots.) | | | | | | | | |
| 1845 | .. | .. | .. | .. | .. | .. | .. | .. |
| 1846 | .. | .. | 2.20 | 2.14 | .. | 2.14 | .. | 2.16 |
| 1847 | .. | .. | 2.34 | 2.38 | 2.40 | 2.42 | 2.44 | 2.40 |
| 1848 | .. | .. | 2.36 | .. | 2.40 | 2.42 | 2.48 | 2.41 |
| 1849 | .. | .. | 1.96 | 1.97 | 2.10 | 2.07 | .. | 2.02 |
| 1850 | .. | .. | 2.16 | 2.28 | 2.25 | 2.25 | .. | 2.23 |
| 1851 | .. | .. | 2.00 | 1.98 | 2.02 | 1.92 | .. | 1.98 |
| 1852 | .. | .. | 2.43 | 2.34 | 2.31 | 2.40 | 2.32 | 2.36 |
| 1853 | .. | .. | 2.30 | 2.34 | 2.29 | 2.28 | .. | 2.30 |
| 1854 | .. | .. | 2.16 | .. | 2.12 | 2.07 | .. | 2.12 |

It is necessary to make a few remarks in reference to this Table of more than one hundred nitrogen determinations. They were made by the method of burning with soda-lime, and collecting and weighing as platinum salt in the ordinary way. Few, perhaps, who have only made a limited number of such determinations, then only on pure and uniform substances, and who have not attempted to control their work at another period, with fresh re-agents, or by the work of another operator, will imagine the range of variation which is to be expected when all these adverse elements are to have their influence. It is freely granted, that the variations shown in the Table between one determination and another, on one and the same substance, are sometimes more than could be desired. The following, however, are the circumstances under which they have been obtained. Experiments 1 and 2 were pretty uniformly made by the same operator, but not all consecutively, or with the same batch of re-agents. It was thought, therefore, that independently of any variations between the two determinations, it would be desirable to have results so important in their bearings, verified by others. Accordingly, samples of each of the ground grains were given under arbitrary numbers, to two other operators, and their results are recorded respectively in columns 3 and 4; and where a fifth determination is given, it is a repetition by one or other of the experimenters last referred to. We should observe, that we have found it almost impossible to procure a soda-lime that will not give more or less indication of nitrogen when burnt with an organic substance not containing it; and hence we have at length adopted the plan of mixing 1-2 per cent. of non-nitrogenous substance intimately with the bulk of soda-lime, igniting it in a muffle, moistening, and reheating it gently. After this treatment the soda-lime is free from ammonia yielding matter. It should further be remembered, that a ground wheat-grain is by no means an uniform substance. Indeed, as we shall show further on, some of the particles of which such a powder is composed, may contain half as much again of nitrogen as others; and thus any inefficiency in the grinding, or error in taking the portion for analysis, may materially affect the result. Notwithstanding all these circumstances, and the admittedly undesirable range of difference in the several determinations in some cases, it will be observed, that generally three at least of the numbers agree sufficiently closely, and in some cases the fourth also. In fact after all, a study of the detailed table, must give considerable confidence, at least in the direction of the variations between the *mean* results given in Table III, and in their sufficiency for the arguments founded upon them. With these remarks on the data, let us proceed with the discussion of Table III itself, which next follows:

TABLE III.

| Particulars of Quantity. | | | Particulars of Quality. | | | | | Composition of Grain. | | | | | | Composition of Straw. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| Total Produce (Corn and Straw) per acre in lbs. | | | Per Cent. Corn in Total Produce. | | Per Cent. Dressed Corn in Total Corn. | | Per Bushel of Dressed Corn. lbs. | | Per Cent. Dry (212°.) | | | Per Cent. Ash in Dry. | | | Per Cent. Nitrogen in Dry. | | | Per Cent. Ash in Dry. | | | Per Cent. Nitrogen in Dry. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Unmanured. | Ammoniacal Salts | Minerals & Ammo- nial Salts. | Unmanured. | Ammoniacal Salts | Minerals & Ammo- nial Salts. | Unmanured. | Ammoniacal Salts | Minerals & Ammo- nial Salts. | Unmanured. | Ammoniacal Salts | Minerals & Ammo- nial Salts. | Unmanured. | Ammoniacal Salts | Minerals & Ammo- nial Salts. | Unmanured. | Ammoniacal Salts | Minerals & Ammo- nial Salts. | Unmanured. | Ammoniacal Salts | Minerals & Ammo- nial Salts. | Unmanured. | Ammoniacal Salts | Minerals & Ammo- nial Salts. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 1545 | 4153 | 6346 | ... | 34.7 | 31.7 | ... | 90.9 | 90.4 | ... | 56.5 | 56.2 | ... | 81.2 | 80.0 | 80.9 | 1.93 | 1.89 | 1.99 | 2.25 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... 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A glance at this Table III, shows that the *quantity* of produce varies very much indeed in one and the same season, according to the manuring. With these great differences in the *quantities*, dependent on manuring, we have far less marked differences in the *quality* of this ripened crop, dependent on the same causes; and this, with some few exceptions, is the same whether we look to the columns indicating the general characters only, or the composition of the produce. That is to say, the same general distinctions between the produce of one season and another, are observable under the several varying conditions of manuring in each, as have been exhibited in the Table I of averages alone. In fact, season, or climatic variations, are seen to have much more influence than manuring, upon the character and composition of the crop.

We have said that, other things being equal, the percentage of nitrogen in our wheat-grain was the lower the more the seed was perfected; and we have also said, that nitrogenous manures greatly aid the development of the crop. But, an inspection of the columns of Table III which give the percentages of nitrogen in the dry substance of the grains produced under the three different conditions of manuring specified, shows us that there is almost invariably, a higher percentage of nitrogen where ammoniacal salts alone have been employed, than where the crop was unmanured. We also see that, almost invariably, there is a higher percentage of nitrogen where mineral manures as well as ammoniacal salts have been used, than in the produce of the corresponding unmanured plots. A closer examination shows, however, though the indication is not uniform, that there is nevertheless, an obvious tendency to a lower percentage of nitrogen, where the mineral constituents also have been employed, than where the ammoniacal salts have been used alone; and with this, there is on the average, a somewhat higher weight per bushel, indicating higher degree of maturation. Then, again, what are the circumstances of these experiments, under which an increased percentage of nitrogen in the fixed substance of the produce, is obtained by a supply of it in manure? The unmanured plot with its low percentage of nitrogen in produce, is shown by the field experiments, to be greatly exhausted of the annually available nitrogen, relatively to the annually available mineral constituents required by the wheat crop. The plot, with the ammoniacal salts alone, is shown by the field results to be defective in the requisite and available minerals, relatively to the available nitrogen, and hence the crop

is grown under a relative excess of the latter. Again, the plots with mineral manures and ammoniacal salts together, received so far an excess of the latter, as to yield, with the minerals, a larger crop than the average of the locality under rotation, and larger also, than the average of seasons would ripen healthily. It is then, under these artificial and abnormal circumstances, of the somewhat unnaturally low percentage of nitrogen, from obvious defect of it in relation to the developing and maturing capabilities of the season on the one hand, and the obviously relative excess of it on the other, that we got an increased percentage of nitrogen in wheat-grain by the use of it in manure. Even under these extreme conditions, the range of variation by manuring is very small; and there is nothing in the evidence that justifies the opinion, that, within the range of full crops and healthy maturation, the percentage of nitrogen in wheat grain, can be increased at pleasure by the use of it in manure. That very opposite extremes of condition of soil-supply, may directly influence the composition even of wheat-grain, is however, illustrated in the percentages of mineral matter, as well as those of nitrogen, given in the table. Thus, taking the mean results only, we have with the relative excess of mineral constituents on the unmanured plot, the highest per cent. in the produce; with the greatest relative defect on the plot with ammoniacal salts only, the lowest per cent. in the grain; and with the medium relation in the other plots, the medium per cent. in the produce. Excepting, however, abnormal conditions, as already remarked, variation in climatic circumstances, has much greater influence on the percentage-composition of wheat-grain, than variation in manuring.

Let us now turn to the composition of the *ash* of wheat-grain. Independently of the defect of a sufficient number of published analyses of wheat-grain ash, a dozen years ago, when we took up the subject, it was then generally believed that the composition of the ash of vegetable produce, would vary considerably with the supplies of the different constituents in the soil; it was thought indeed, that according to the abundance of their presence, one base might substitute another, as for instance *soda*, *potash*, and so on. About the same time that we undertook a series of wheat-ash analyses, the ashes of various succulent vegetables were also analysed. This latter investigation led us to conclude, that the fixity of the composition of the ash of such substances, depended very much upon the degree of maturation of the produce; and in

fact that some constituents—soda and chlorine for instance—occurred in much larger quantities in the more succulent and unripe, than in the more elaborated specimens. It seemed to be perfectly consistent with this experience, to find in the ash of a comparatively perfected vegetable product like wheat-grain, a considerable uniformity of composition—such indeed as the analyses now to be recorded will indicate.

These analyses were made ten years ago by Mr. Dugald Campbell, and the late Mr. Ashford. And as, since that time, the methods of ash-analysis have in some points been improved upon, it will be well to give an outline of the plan then adopted: especially as it is by a consideration of the tendencies to error on some points, that we must interpret the bearings of the actual figures given. On this point we need only add, that Mr. Campbell fully concurs in the tenor of our remarks.

Method of Analysis:—Three portions of ash were taken.

No. 1. In this the sand, silica, and charcoal, phosphate of iron, phosphoric acid, lime, and magnesia, were determined. The ash was dissolved in dilute hydrochloric acid, evaporated to perfect dryness, moistened with hydrochloric acid, boiled with water, and the insoluble matter collected and weighed, as—*sand, silica, and charcoal*. To the filtrate, acetate of ammonia was added, and after digestion, the precipitate separated, dried, ignited and weighed—as *phosphate of iron*. To the filtrate now obtained, a solution of a weighed portion of pure iron dissolved in nitro-hydrochloric acid was added, then acetate of ammonia, and the mixture digested until the whole of the iron was precipitated as phosphate of the peroxide with excess of peroxide, from which was calculated the *phosphoric acid*. From the solution filtered from the phosphate of iron and oxide of iron, the *lime* was separated as oxalate and ignited as carbonate; and from this last filtrate, the *magnesia*, by phosphate of soda and ammonia.

No. 2. A second portion of ash was put into a carbonic acid apparatus, the acid, if any, evolved by means of nitric acid, and determined by the loss. The solution being filtered, sulphuric acid was separated by nitrate of baryta; and afterwards *chlorine* by nitrate of silver.

No. 3. To a solution of a weighed portion of the ash in hydrochloric acid, caustic baryta was added in excess, and the precipitate separated by filtration; the excess of baryta was then

removed by carbonate of ammonia, and the filtered solution evaporated to dryness, the residue heated to redness and weighed; water added, any insoluble matter deducted, and the remainder taken as chlorides of potassium and sodium; a solution of chloride of platinum was now added to separate the *potash*; the *soda* being calculated from the loss.

It is now admitted, that the separation of phosphate of iron from the earthy phosphates by acetate of ammonia as above described, is unsatisfactory; and it is probable the amounts given in the tables as phosphate of iron are too high, and if so, part of the difference should obviously go to the earthy bases. For a similar reason it is possible that the phosphoric acid determinations may be somewhat too high—also at the expense of the earthy bases. Then again, it is well-known that in practice the process for potash and soda, is one of some delicacy; and that the tendency of manipulative error is to give the soda somewhat too high. We conclude upon the whole, that our phosphoric acid determinations *may* be somewhat high; our phosphate of iron pretty certainly so; and probably the soda also; the other bases being, on this supposition, given somewhat too low.

The wheat-grain ash-analyses, 23 in number, and referring to the produce of three separate seasons, and of very various manuring, are given in the following Tables—numbered IV, V and VI respectively.

TABLE IV.
Analyses of Wheat-Grain Ash.

| Plot Numbers | 2 | 3 | 5 | 1 | 9 | 15 | 16 | 18 | Means. |
|---|----------------------------|------------|-------------------------------|--|---|--|--|--------------------------------|--------|
| Manuring, per acre | Farm-yard Manure; 14 tons. | Unmanured. | Superphosphate Lime, 700 lbs. | Superphosphate Lime, 700 lbs. Rape Cake, 150 lbs. | Superphosphate Lime, 616 lbs. Sulphate Ammonia, 165 lbs. | Superphosphate Lime, Potash and Magnesia, and Silicate Potash. | As 15, with Soda and Sulphate Ammonia, 65 lbs. | As 16, and Rape-Cake, 15½ lbs. | |
| | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Characters of the produce:— | | | | | | | | | |
| Per Cent. Corn in Total Produce | 46·4 | 45·2 | 46·1 | 46·4 | 48·3 | 46·9 | 46·8 | 43·6 | 46·2 |
| Weight per bushel of Dressed Corn (lbs.) | 59·2 | 58·5 | 58·2 | 59·0 | 62·2 | 62·0 | 62·5 | 62·0 | 60·4 |
| Per Cent. Dry Substance in Corn (at 212°) | 82·8 | 81·8 | 81·1 | 82·3 | 83·6 | 83·1 | 83·3 | 83·2 | 82·65 |
| Per Cent. Ash in Dry Substance | 2·06 | 2·17 | 2·25 | 1·88 | 2·00 | 2·02 | 2·03 | 1·96 | 2·05 |
| Constituents of Ash:— | | | | | | | | | |
| Phosphoric Acid | 48·13 | 50·84 | 51·02 | 50·48 | 49·92 | 50·39 | 51·43 | 49·28 | 50·16 |
| Phosphate of Iron | 2·56 | 2·45 | 2·62 | 2·10 | 2·32 | 3·00 | 2·54 | 2·75 | 2·54 |
| Potass | 28·91 | 30·22 | 29·37 | 27·40 | 29·06 | 29·09 | 28·33 | 28·33 | 28·93 |
| Soda | ·76 | ·00 | ·22 | 1·12 | ·90 | ·00 | ·00 | 2·10 | ·57 |
| Magnesia | 11·84 | 11·04 | 11·81 | 10·10 | 10·84 | 10·86 | 11·38 | 11·38 | 11·07 |
| Lime | 3·77 | 3·00 | 3·18 | 2·71 | 3·39 | 3·17 | 3·31 | 3·48 | 3·30 |
| Chlorine | Traces | ·12 | Traces | ·52 | ·15 | ·09 | ·21 | Traces | ·13 |
| Silica, Sand, and Charcoal | 2·64 | 2·72 | 1·49 | 5·45 | 2·57 | 1·86 | 1·47 | 1·70 | 2·45 |
| Totals | 98·61 | 100·39 | 99·71 | 99·88 | 99·15 | 98·46 | 98·67 | 99·22 | 99·15 |

TABLE VI.
Analyses of Wheat-Grain Ash.
HARVEST, 1846.

| Plot Numbers | .. | .. | .. | 2 | 3 | 1 | 8 B | 4 | 11 B | Means. |
|---|----|----|----|-------------------------------|------------|-----------------------|---|--|--|--------|
| Manuring, per acre | .. | .. | .. | Farm-yard Manure, 14 tons. | Unmanured. | Bone-ash, 224 lbs. | Bone-ash, 224 lbs. Sulphate and Muriate Ammonia, each 112 lbs. | Bone-ash, 224 lbs. Hydrochloric Acid 224 lbs. Sulphate Ammonia, 224 lbs. | Bone-ash, 224 lbs. Sulphuric Acid, 224 lbs. Sulphate and Muriate Ammonia, each 112 lbs. | |
| | | | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |
| Character of the produce:— | | | | | | | | | | |
| Per Cent. Corn in Total Produce | | | | | | | | | | |
| Weight per bushel of Dressed Corn (lbs.) | | | | | | | | | | |
| Per Cent. Dry Substance in Corn (at 212°) | | | | | | | | | | |
| Per Cent. Ash in Dry Substance | | | | | | | | | | |
| Constituents of Ash:— | | | | | | | | | | |
| Phosphoric Acid | | | | | | | | | | |
| Phosphate of Iron | | | | | | | | | | |
| Potass | | | | | | | | | | |
| Soda | | | | | | | | | | |
| Magnesia | | | | | | | | | | |
| Lime | | | | | | | | | | |
| Chlorine | | | | | | | | | | |
| Silica, Sand, and Charcoal | | | | | | | | | | |
| Totals | | | | | | | | | | |

* It would seem probable that in these two cases the Lime is given too low; but as the analyst, Mr. Aslford, is dead, no reference can be made, and we have unfortunately not had time to repeat the analyses prior to publication, as we had intended.

It is at once seen, that this ash may be reckoned to contain neither sulphuric acid, carbonic acid, nor chlorine. The latter at least occurred only occasionally, and then in such small quantities, as to lead us to the supposition that its presence is accidental, or at any rate not essential, in the ash of a perfectly-ripened grain. From the frequent absence of soda again, and from the uncertainty in its determinations as above alluded to, we are led to look at it as an equally unessential ingredient in the grain-ash of perfectly ripened wheat. Excluding then the chlorine, the soda, the iron of the phosphate of iron, and that portion of the matter collected as insoluble, which may have been soluble silica—the whole of these, on the average, amounting to a very few per cent.—the ash of wheat-grain is seen to consist essentially of *phosphates only*; the bases being potash, magnesia, and lime. The potash amounts to nearly one-third of the whole ash; the magnesia to rather more than one-third of the potash; and the lime to about one-third of the magnesia.

If we now compare with one another the analyses of the eight different ashes in 1844, those of the seven in 1845, or of the six in 1846, having regard to the manures by which the crops were grown, it is impossible to say that these have had any direct and well-defined influence upon the composition of the ash of the grain. Thus we find, looking at the Table for 1844, that several of the plots manured with superphosphate of lime, yield a grain-ash having no higher percentage of phosphoric acid than that of the unmanured plot. Again, where potash is added (plots 15, 16, and 18), the percentage of it in the ash is not greater than the average of the cases where it was not employed. And again, in the only case where soda was employed (plot 16), there is none of it found in the ash; nor, lastly, is the percentage of magnesia obviously increased by the use of it in manure. A similar detailed consideration of the composition of the ashes of the seasons of 1845 and 1846, would, as already intimated, lead to a similar conclusion. In fact, the variations in the composition of the ash of this supposed ripened product, according to the manure by which it is grown, seem to be scarcely beyond the limits of error in the manipulation of the analysis; though, one case at least of the duplicate analysis of the same ash—namely, that of No. 9, 1844—indicates the range of variation from this cause to have been but small; in the other, (No. 17, 1845) it was somewhat greater.

Although the accuracy of the analyses may not be such as to

show the difference in composition, if any, dependent on *manure*, yet it is found to be quite adequate to indicate the marked differences in the *degree of development and maturation* of the grains, dependent upon *season*. Before calling attention to the figures illustrating this point, it should be remarked that the season of 1845 was the worst but one, and that of 1846 nearly the best, for ripening the grain, during the thirteen years of our continuous growth of wheat. And we shall find, consistently with this, and with the conclusions arrived at in connection with Tables I and III, that the variation in the composition of the ash is, comparing one year with another, much the greatest in the produce of the bad ripening season 1845, and much the least in the good ripening season 1846. This point, and some others, are illustrated in the following Summary Table, No. VII.

TABLE VII.

Composition of Wheat-Grain Ash.

| | Variation in per Cent. in each Season. | | | | Mean for each Season. | | | Means according to Manuring. | | | | General Means. | | | |
|---|--|----------|----------|----------|-----------------------|----------|----------|------------------------------|-------|-------|------------------------------|-----------------------------------|---|----------------------------------|--------------------------|
| | 1844 | | 1845 | | 1846 | 1844 | | 1845 | | 1846 | Unma- nured (3 years). | Farm-yard Manure (3 years). | Other Manures (3 years), 17 Cases. | 23 Cases, Rotham- sted. | 26 Cases, Mr. Way. |
| | 9 Cases. | 8 Cases. | 8 Cases. | 6 Cases. | 9 Cases. | 8 Cases. | 6 Cases. | | | | | | | | |
| Characters of the produce :— | | | | | | | | | | | | | | | |
| Per Cent. Corn in Total Produce | .. | .. | .. | .. | 46.2 | 34.1 | 43.3 | 41.4 | 40.8 | 41.3 | 41.2 | | | | |
| Weight per bushel of Dressed Corn (lbs.). | .. | .. | .. | .. | 60.4 | 57.0 | 63.3 | 59.6 | 59.6 | 60.1 | 60.0 | | | | |
| Per Cent. Dry Substance in Corn (at 212°) | .. | .. | .. | .. | 82.6 | 80.9 | 84.1 | 82.3 | 82.3 | 82.5 | 82.4 | | | | |
| Per Cent. Ash in Dry Substance | .. | .. | .. | .. | 2.05 | 1.92 | 1.98 | 2.04 | 2.01 | 1.97 | 1.99 | | | | |
| Composition of Ash :— | | | | | | | | | | | | | | | |
| Phosphoric Acid | 3.30 | 5.87 | 1.89 | 49.80 | 50.16 | 49.05 | 49.81 | 49.81 | 48.41 | 49.88 | 49.68 | | | | 45.01 |
| Phosphate of Iron | .90 | 3.87 | 1.45 | 2.43 | 2.54 | 2.10 | 2.14 | 2.14 | 2.06 | 2.45 | 2.36 | | | | 0.82 |
| Potass | 2.82 | 7.11 | 3.07 | 29.72 | 28.93 | 29.54 | 29.72 | 29.78 | 28.03 | 29.50 | 29.35 | | | | 31.44 |
| Soda | 2.10 | 8.01 | .85 | .10 | .57 | 2.49 | .08 | .08 | 3.04 | .95 | 1.12 | | | | 2.71 |
| Magnesia | 1.74 | 2.60 | .79 | 10.78 | 11.07 | 10.24 | 10.78 | 11.20 | 11.31 | 10.51 | 10.70 | | | | 12.36 |
| Lime | 1.06 | 1.64 | 1.74 | 3.84 | 3.30 | 3.18 | 3.15 | 3.15 | 3.47 | 3.43 | 3.40 | | | | 3.52 |
| Sulphuric Acid | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | | | | 0.34 |
| Carbonic Acid | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | | | | 0.02 |
| Chlorine | .. | .. | .. | .17 | .13 | .10 | .14 | .14 | .04 | .14 | .13 | | | | .13 |
| Silica, Sand, and Charcoal | .. | .. | .. | 2.40 | 2.45 | 2.55 | 2.76 | 2.76 | 2.60 | 2.41 | 2.47 | | | | 3.67* |
| Totals | .. | .. | .. | 99.24 | 99.15 | 99.25 | 99.06 | 99.06 | 98.96 | 99.27 | 99.21 | | | | 100.03 |

* Mr. Way gives this as soluble silica, exclusive of the sand and charcoal included with it in our own analyses.

Looking at the first Division of this Table VII, it is seen that in the item of *phosphoric acid*, the variation in the percentage among the several cases in each year, is the greatest in 1845, and the least in 1846; in the *phosphate of iron*, it is the greatest in 1845; in the *potash*, it is the greatest in 1845, much less and about equal, in 1844 and 1846; in the *soda*, it is much the greatest in 1845, and much the least in 1846; in the *magnesia*, it is again far the greatest in 1845, and it is the least in 1846. In the case of the *lime*, we have an exception to this general indication, dependent on the two low amounts of it given for Nos. 2 and 3, 1846; but if these are really in error in the direction suggested at the foot of Table VI, the indication would be the same as for the other constituents. We have then in the circumstances of the seasons, and in the comparative characters of the produce coincident with these variations, the evidence that for one and the same description of grain, in a perfectly matured condition, the composition of the ash will be, within certain narrow limits, constant.

So far as the constituents of the ash of the entire grain of wheat is concerned, we have only further to call attention to the three other Divisions of this Summary Table No. VII. In these are shown, side by side:—

In the second Division of the Table, the mean composition of the ashes for each of the three separate years;

In the third Division, the mean composition for the three years together: (a) of the grain-ash from the unmanured plot—(b) of that from the farm-yard manured-plot—(c) of the grain-ashes from all the other manures during the three years, including 17 cases; and

In the fourth and last Division, the mean composition of all our own wheat grain-ashes analyzed, 23 in number, by the side of the mean of 26 analyses of the grain-ashes of wheat, of different descriptions or grown in different localities, published by Mr. Way.

We will go into very little detail discussions of these mean results, as the points they illustrate have most of them already been alluded to. We may first remark, as a point to which we shall recur further on, that the mean percentage of *lime*, is the least in the bad year 1845, and the greatest in the good year 1846. Again, it is greater in the average from the manured plots, than in that from the unmanured. We may perhaps here anticipate by saying, that this is at any rate consistent with what we shall

afterwards have to record, namely, that the ash of the finer flour—of which there is a greater proportion in the grain of the seasons of best maturation—contains more lime than that of the coarser and more branny portions of the grain.

Lastly, in reference to this Summary Table, we would call attention to the mean composition of wheat grain-ash yielded by the 26 analyses given by Mr. Way, by the side of that of the 23 specimens grown at Rothamsted. Mr. Way's analyses, equally with our own, show that wheat grain-ash essentially consists of phosphates of potash, magnesia, and lime. He, however, if we exclude silica, gives higher percentages of base, and a lower one of acid, than our own analyses indicate. Mr. Way's average amount of phosphoric acid is indeed nearly 5 per cent. less in the ash than ours. His series, however, included many descriptions of wheat, and our own only one—the Old Red Lammas. In several of his cases, too, we observe that the percentage of this acid very closely approximates to our own average.

We have now given a summary view of some points of the composition of the entire wheat-grain, and of its ash, as affected by varying season, and various manuring. We next turn to an equally summary statement, of a large number of experiments made in reference to the *yield*, and *composition*, of the various products separated in the milling process. The grains operated upon with this view, were of the same description of wheat, but grown experimentally in different seasons, and under different conditions of manuring.

There have been many observations recorded as to the percentage of flour obtained in practice from 100 parts of grain, and in a subsequent Table some of these will be adduced. We are also indebted to M. Boussingault for the determination of the flour and of the bran, yielded by 24 different descriptions of wheat, all grown side by side in the Jardin des Plantes at Paris. His method was to powder the grains in a mortar, and separate the flour and bran by means of a silken sieve. Results of this kind can, perhaps, scarcely be compared with those of the ordinary mill. The differences exhibited between the different specimens were indeed very great; but the comparisons afforded within the series itself are interesting and very curious.

In our own experiments, the so-called *Colonist's steel hand-mill* was first had recourse to; as it was thought that by its use, rather

than that of an ordinary flour-mill, much smaller quantities of grain might be submitted to experiment, and that uniformity of working would also be more within our control. It was soon found, however, that in all cases the grain was, in this steel-mill, rather cut up than crushed and rubbed down, as between ordinary mill-stones. It was also found, that the action in this respect varied considerably according to the speed of the operator, and to the precise set of the mill, which required to be varied according to the character of the grain. From these causes a statement of the *amount of the yield*, of the various products obtained from the steel hand-mill, would be of little value. Though further on we shall have to call attention to some interesting points connected with the comparative composition of the several products of the grains mechanically separated in this way.

We next determined to submit a series of the experimentally grown grains, to careful, and as far as possible, uniform treatment between the stones, and in the dressing apparatus, of an ordinary flour-mill. The mill in question was worked by water-power. From 125 to 250 lbs. of the several grains were submitted to the experiment; the whole of the apparatus being carefully cleared of the products of one specimen before another was commenced upon. The weights and samples of the "*meals*" as furnished by the stones, and of the several products separated in the dressing-machine, were taken under our own personal superintendence. Even here, and although every possible precaution was taken, considerable irregularities in the action of the apparatus were manifest, depending partly on the varying characters of the grain. Indeed it was clear, that to obtain results as to comparative yield of flour, strictly referable to the practical qualities of the respective grains, it would be necessary to operate on much larger quantities of each than those even now taken, in order that the miller might so re-adjust the set of his stones, as the work proceeded, according to the character of the grain and of the meal which it afforded, as to get from each its largest yield, as he would do in working upon considerable quantities. In all, twenty-eight lots of grain were operated upon in this way; and although, as above implied, and as will be pointed out further on, the results might in some points have been somewhat different with larger quantities, yet the miller, after a careful examination of all the products, decided that their general bearings were to be fully trusted.

In some cases the meal obtained from the stones was separated

in the dressing apparatus into nine products, and in others the products of the first three wires were taken together, constituting the bulk of the *fine* flour obtainable, and amounting to only about 70 per cent. of the grain. In practice, however, the fourth product of the dressing machine, "*Tails*," is generally redressed, and the fifth, "*Fine Sharps*" or "*Middlings*," reground and redressed, together raising the amount of good bread-flour to about 80 per cent., or sometimes more. The sixth product is called "*Coarse Sharps*;" the seventh, "*Fine Pollard*;" the eighth, "*Coarse Pollard*;" and the ninth, "*Long Bran*." It should be stated, however, that mills vary very much in the arrangement of their dressing machines in different localities, and even in the same locality; so that the exact division of the products here given, will not apply invariably.

In Table VIII are given—

1st. In the upper division of the Table, the percentage yield in 100 meal, of each of the mill products, 7 or 9, as the case may be; each figure being the mean of several experiments.

2nd. (In the middle division of the Table)—The mean per cent. of dry substance (at 212°), in each flour, bran, &c. And,

3rd. The mean per cent. of mineral matter (ash), in each of the same mill products.

As will be seen, seven of the specimens were grown in 1846, nineteen in 1847, and two in 1848; and in order to give some idea of the general character of the produce yielding the results in each of the separate columns, there is given at the head the mean bushels per acre, the mean weight per bushel, and the mean per cent. of corn in total produce, of the specimens to which the column refers.

After the remarks already made, little need be said in detail regarding the comparative yield of the various products by 100 parts of the different meals. It was decided by the miller, that pretty uniformly there was too much flour left in the fourth, but particularly in the fifth product; and this, as an inspection of the Table will show, was obviated in the later experiments, namely, those on the grain of the harvest 1848. So far, then, the variation of the result is more due to the management of the miller, than to the intrinsic character of the grain.

It is more interesting to observe, that a very careful examination of all the products led to the conclusion, that the grains grown by the more nitrogenous manuring, and consequently in the larger crops, *provided they were well developed and matured*,* allowed a better separation of the flour, and less cutting up and intermixture of branny particles with it; and hence, yielded a cleaner bran than the grain of the poorer crops. This was not the case, however, unless the highly-manured crops were at the same time well developed. It is consistent with this character of the grain of the more highly-manured crops, that the produce of the heavier and richer wheat-lands is generally admitted to yield a larger proportion of flour. The fact that the grain of richly-manured crops is frequently coarse, and not the good miller's sample, arises from the circumstance, not of the direct effect of rich manuring in depreciating the quality of the grain, but because the larger crops are more subject to injury due to climatic circumstances, and are consequently frequently less favourably developed and matured.

It will be observed, that the amount of long bran is always more than 2, and in the year of badly-ripened grain (1848), it is nearly 6 per cent. of the total meal. This ninth product, together with the three or four immediately before it in the list, yield us nearly 20 per cent. of the total meal, of such a branny character as seldom to be used for human food. Some of the more recent experimenters, MM. Millon and Peligot for example, have concluded that the amount of actual woody fibre in wheat-grain is seldom more than from 2 to 3 per cent. On this supposition, the nearly 20 per cent. of the grain generally not applied directly as human food, would contain but a small proportion of necessarily indigestible woody matter; and it would appear that there was very great room for improvement in the modes of preparation of the grain, if

* It would appear that, in a good ripening season, this condition is best attained when the crop is cut before the grain is perfectly ripe.

it were desirable to separate as human food in the first instance, a larger proportion of its nutritious matters. M. Poggiale, on the other hand, maintains that the quantity of woody fibre refractory to the digestive organs, though not to chemical agents out of the body, is really very considerable.* But, of some points of the composition of the various products, we shall have to speak more in detail presently.

In the second or middle division of Table VIII, we have the average percentage of dry matter in the different products. In reference to these results it may be noticed, that, as might be expected, the percentage of dry matter is rather higher in the mill products, than it was in the entire grains which yielded them. This is particularly the case in regard to the two specimens of the harvest 1848, the mill products of which give, on the average, a higher per cent. of dry matter than the samples of either of the other two years, although the dry matter of the entire grain of that season (1848), was very low. The differences are therefore obviously more due to the circumstances of preservation and after-treatment, than to distinctions in the character of the respective grains. The only other remark which need be made regarding the varying percentages of dry matter, is, that the branny, or more external portions of the grain, have pretty uniformly a higher percentage of dry matter than the more farinal internal portions.

The widely differing percentages of *mineral matter* in the several mill-products of the same grain, and the variations in this respect, even between the corresponding products in the different specimens, in the same, or in different seasons, are both more striking, and of greater interest.

It is seen, that we have about ten times as high a percentage of ash in the ninth product, or bran, as in the first three, or purer flours. The percentage increases rapidly from the fourth to the ninth—that is to say, the greater the proportion of branny particles. A careful examination of the more detailed Tables also showed, that the variations in the percentage of mineral matter in the corresponding products of different specimens of grain, had a direct relation to the percentage, or relative position of the respective products, in the 100 of meal; in other words, to the

* Since the above was written, a very favourable report has appeared in the "Comptes Rendus" (January 12, 1857), by MM. Dumas, Pelouze, Payen, Peligot, and Chevreul—the Commission appointed by the Academy of Sciences, to inquire into the matter—on a new process of M. Mège Mouriès, which claims to yield a perfectly white, wholesome, and agreeable bread, employing 86–88 per cent. of the entire grain.

proportions of flour or of bran which they respectively contained. Although, however, the *percentage* of mineral matter is so very much greater in those portions of the grain which are not generally used in the first instance as human food, yet, an inspection of the last column of the Table, showing the *distribution* of the mineral matter in the several products of 100 of meal, according to the amount of each of these, will show that, even in our first three products, we have nearly one-third of the whole mineral matter of the grain; and adding to these a certain portion of that in the fourth and fifth products, which frequently contribute to the bread-flour, we shall have more than one-third of it in the currently edible portion of the grain. Further information as to the composition of the respective mill-products, and of their ashes, will be found in Tables IX, X, XI, and XII.

In Table IX are given the individual nitrogen determinations in each of the several mill-products; those in the first three columns being by one experimenter, and those in the fourth column by another. In Table X is given a collective view of the composition of the same products, in regard to some other constituents, as far as they have been determined; including also the mean results of Table IX.

TABLE IX.

Determinations of Nitrogen per Cent. in Mill Products of
Wheat-Grain.

HARVEST 1846; GROUND 1848.

| Description of Mill Products. | In natural state of dryness. | | | | |
|---------------------------------|------------------------------|-------|------|------|-------|
| | Experiments. | | | | Mean. |
| | 1. | 2. | 3. | 4. | |
| 1. Wire 1 | 1.59 | 1.69 | 1.62 | .. | 1.63 |
| 2. „ 2 | 1.64 | 1.73 | 1.69 | .. | 1.69 |
| 3. „ 3 | 1.77 | 1.78 | 1.79 | .. | 1.78 |
| 4. Tails | 1.88 | 1.86 | 1.84 | .. | 1.86 |
| 5. Fine Sharps, or Middlings .. | 2.20 | 2.20 | 2.22 | 2.22 | 2.21 |
| 6. Coarse Sharps | 2.58 | 2.52 | 2.59 | 2.62 | 2.58 |
| 7. Fine Pollard | 2.43 | 3.37 | 2.48 | 2.48 | 2.44 |
| 8. Coarse Pollard | 2.41 | 2.32 | 2.47 | 2.46 | 2.42 |
| 9. Long Bran | 2.37 | 2.37* | .. | 2.42 | 2.39 |

* By a third experimenter.

TABLE X.
Composition of Mill-products of Wheat Grain.
HARVEST 1846; GROUND 1848.

| Description of Mill Products. | Flours, &c. from 100 Grain. | In 100 of each Product. | | | In 100 each Ash. | | Distribution of Constituents in Mill Products of 100 Grain. | | | |
|---------------------------------|-----------------------------|----------------------------|-----------------------|-----------|--------------------|------------------|---|-----------|--------------------|------------------|
| | | Dry Substance (at 212° F.) | Mineral Matter (Ash). | Nitrogen. | Insoluble in Acid. | Phosphoric Acid. | Mineral Matter. | Nitrogen. | In the Ash. | |
| | | | | | | | | | Insoluble in Acid. | Phosphoric Acid. |
| 1. Wire 1 .. | 51.2 | 85.5 | 0.71 | 1.63 | 6.04 | 44.3 | 0.36 | 0.83 | 0.022 | 0.161 |
| 2. " 2 .. | 24.8 | 85.6 | 0.74 | 1.69 | 5.83 | 45.5 | 0.18 | 0.42 | 0.010 | 0.083 |
| 3. " 3 .. | 1.7 | 85.0 | 0.82 | 1.78 | 5.74 | 48.1 | 0.01 | 0.03 | 0.000 | 0.007 |
| 4. Tails .. | 1.6 | 85.2 | 1.04 | 1.86 | 2.18 | 48.4 | 0.02 | 0.03 | 0.000 | 0.008 |
| 5. Fine Sharps, or Middlings .. | 3.3 | 85.5 | 2.19 | 2.21 | 3.04 | 51.3 | 0.07 | 0.07 | 0.002 | 0.037 |
| 6. Coarse Sharps .. | 3.3 | 86.1 | 3.93 | 2.58 | 3.84 | 49.6 | 0.13 | 0.08 | 0.005 | 0.064 |
| 7. Fine Pollard .. | 1.8 | 86.5 | 5.46 | 2.44 | 0.84 | 52.3 | 0.10 | 0.04 | 0.001 | 0.051 |
| 8. Coarse Pollard .. | 6.7 | 86.1 | 6.56 | 2.42 | 0.56 | 55.2 | 0.44 | 0.16 | 0.002 | 0.242 |
| 9. Long Bran .. | 5.0 | 86.4 | 7.14 | 2.40 | 0.60 | 54.8 | 0.36 | 0.12 | 0.002 | 0.195 |
| Totals .. | 99.4 | .. | .. | .. | .. | .. | 1.67 | 1.78 | 0.044 | 0.850 |

The grain to which Tables IX and X refer, was an equal mixture of the produce from four different plots, very variously manured, and grown in the season 1845-6; the harvest of which yielded one of the best-matured grains throughout our series of field experiments. The wheat in question was, however, not ground until 1848; and we have in the percentage-yield of the respective products, confirmation of the general opinion, that other things being equal, old wheat yields up its flour better than new. Thus, whilst in the average of the cases already recorded, we have little more than 70 per cent. of flour through the first three wires, we have from this old wheat $77\frac{3}{4}$ per cent. The products 4 and 5, from which a further yield of bread-flour is obtained, were correspondingly small; but Nos. 8 and 9 were, on the other hand, somewhat large.

The particulars given in Table X are the percentages of *Dry Matter*, of *Ash*, and of *Nitrogen*, in the respective mill-products of this mixed grain. There are also given the percentages of *Matter insoluble in Acid*, and of *phosphoric acid* in each of the nine ashes; and in the last four columns we have the *distribution* of the total mineral matter, of the nitrogen, and also of the insoluble matter, and phosphoric acid of the ash, in each of the nine products, according to the proportion of the latter in 100 of the grain or meal.

The percentage of *Dry Matter* in the several products from this old grain is, as would be expected, somewhat higher than the average from the grains of the same year which had not been so long stored. As before, the percentage of Dry Matter shows a tendency to increase as we proceed to the outer portions of the grain. The percentages of ash also show the same relations as already pointed out.

Referring to the column of the percentage of nitrogen in each of the nine separated products, we find that it is lowest in the products at the head of the dressing machine—that is, in the flours; and it is half as high again in the more branny portions. It is seen, however, to be the highest of all in the product No. 6; and somewhat lower in the coarser brans. It may be remarked, that the indications of the figures in this respect are at any rate consistent with such observations as have been recorded regarding the structural composition of wheat-grain; it being stated that the greatest concentration of nitrogenous compounds is immediately below the pericarp itself; and we should expect that the

longer bran would have less of the more internal matters adherent to it.

The higher percentage of nitrogen in bran than in fine flour, has frequently led to the recommendation of the coarser breads as more nutritious than the finer. We have already seen that the more branny portions of the grain, also contain a much larger percentage of mineral matter. And further, it is in the bran that the largest proportion of fatty matter—the non-nitrogenous substance of highest respiratory capacity which the wheat contains—is found. It is, however, we think, very questionable whether, upon such data alone, a valid opinion can be formed of the comparative values as food, of bread made from the finer or coarser flours from one and the same grain. The published evidence at command leads to the conclusion, that of the nitrogenous constituents of bran, a much larger proportion is soluble in water, than of those in the finer flours. That is to say, there is in the bran, probably, a larger proportion of the more universal vegetable compound, albumen, and less of those more special to the grain of wheat; and hence we may perhaps conclude, that it exists in a less elaborated, and probably, therefore, less assimilable condition.* It is stated, on the other hand, by Poggiale, that a large proportion of the insoluble nitrogenous constituents of bran, occurs in a form only in an inferior degree digestible. Again, it is an indisputable fact, that branny particles, when admitted into the flour in the degree of imperfect division in which our ordinary milling processes leave them, very considerably increase the peristaltic action; and hence the alimentary canal is cleared much more rapidly of its contents. It is also well known, that the poorer classes almost invariably prefer the whiter bread; and among some of them who work the hardest, and who consequently would soonest appreciate a difference in nutritive quality (navvies for example), it is distinctly stated, that their preference for the whiter bread is founded on the fact, that the browner passes through them too rapidly; consequently, before their systems have extracted from it as much nutritious matter as it ought to yield them.

* According to M. Mège Mouriès, before referred to, a portion of the soluble nitrogenous matter of bran exists as a peculiar body, *Cerealine*, which when dissolved up from bran in water at a given temperature, effects the solution of the adherent starch also. His process of extracting from the bran an additional amount of the bread-material which the grain contains, consists in fermenting, after the addition of some glucose, an infusion of the finer brans, straining off the woody matter, and using the fluid in making up the dough with the finer flour.

It is freely granted, that much useful nutritious matter is, in the first instance, lost as human food, in the abandonment of 15 to 20 per cent. of our wheat-grain to the lower animals. It should be remembered, however, that the amount of food so applied, is by no means entirely wasted. And further, we think it more than doubtful, even admitting that an increased proportion of mineral and nitrogenous constituents would be an advantage, whether, unless the branny particles could be either excluded, or so reduced as to prevent the clearing action above alluded to, more nutriment would not be lost to the system by this action, than would be gained by the introduction into the body coincidentally with it, of a larger actual amount of supposed nutritious matters. In fact, all experience tends to show, that the *state*, as well as the chemical composition of our food, must be considered; in other words, that its digestibility, and aptitude for assimilation, are not less important qualities, than its ultimate composition. Observation also tends to show, that elaboration, or maturation, have their influence in determining the digestibility or the assimilability of our food—both the vegetable and animal. But to this point we shall refer again presently.

Returning to the experimental results in Table X, the next point of remark is as to the amount of matter *insoluble in acid*, in the ash of the respective mill-products. It is seen, that the percentage of such matter is very much greater—indeed in this particular case, ten times greater—in the ash of the finest flour, than in that of the coarsest bran. It was at first thought that this must be an error. Some repetitions were therefore made, and the products of the steel-hand-mill were also examined; when it was found that the result in question was fully confirmed. It would be interesting to examine the series, to determine what proportion of this insoluble matter is really proper mineral constituent of the respective products, and how much adventitious merely. On consideration, it will however be clear, that the process of dressing the meal would tend to shake and clean the bran, from all adherent matters; which, if silicious, as well as the particles arising from the abrasion of the mill-stones, would naturally be found among the heavier products at the head of the machine. That is to say, they would be found in larger proportion in the flour, whilst the bran, by the mechanical methods of its separation, would be almost entirely freed from them. According to published analyses, it would appear, however, that *silica*, as

distinguished from merely insoluble sandy matter, does exist to a considerable, though variable extent, in the ash of entire wheat-grain. And from the results now given, it may perhaps be concluded, that this constituent found to exist so constantly in some animal substances, does really occur in larger amount in those portions of wheat-grain which are best adapted as food?

Phosphoric acid, on the other hand, is seen to be in smallest proportion in the ash of the flour at the head of the dressing machine; and the percentage pretty gradually augments as we proceed from the finer to the coarser and more branny portions, the ash of the latter being far the richest in this essential acid.*

It may further be remarked in reference to the varying composition of the ash of the different mill-products, that in several series we have found the *magnesia* greatly to increase as we proceed from that of the finer to that of the coarser products. The percentage of *lime* is, on the other hand, greatest in the ash of the flours, and less in that of the brans. This latter point is consistent with a tendency discernible, to an increase in the percentage of lime in the ash of those grains most matured in one and the same season, or in the ash of the grains grown in a season of higher maturing character. We may further conclude, from the great increase in the percentages both of the phosphoric acid, and of the *magnesia*, as we proceed from the ash of the flours to that of the brans, and also from the very slight compensation from the decrease in that of the lime (the total amount of lime being relatively small), that the chief complementary constituent of wheat-grain ash—namely, *potash*—will occur in larger proportion in the ash of the flours than in that of the brans; hence, its larger amount will be coincident with the larger amount of silica.

In the last Division of Table X is shown the *distribution* in the respective products from 100 of grain, or its meal—of the nitrogen, of the total mineral matter, and of the insoluble substance and phosphoric acid of the latter—which the entire grain contained.

It will be seen, that notwithstanding the percentage of nitrogen is so much greater in the branny products, yet owing to the smaller amount of these, by far the larger proportion of the total nitrogen of the grain is accumulated in the flours. In fact, in the case

* Probably a portion of the phosphoric acid existing in wheat-grain-ash is due to the oxidation, during incineration, of phosphorus, found by Professor Voelcker to exist in such large amount, associated with the nitrogenous bodies. See also Professor H. Rose on this subject—Poggendorff's *Annalen*, vol. lxxvi. p. 305.

before us about three-fourths of the nitrogen would be accumulated in those of the products which would be ordinarily used for bread, or for human food in other forms. On the other hand, only about two-fifths of the total mineral matter would be found with this three-fourths of the nitrogen. Of the *phosphoric acid* again, the larger amount is distributed in the branny portions; only about one-third of it being obtained in the bread flours. At the foot of these columns of the distribution of the constituents, the percentage in the entire grain or meal of the items as determined by analysis in each separate product, is given by the addition of these items so obtained; and the percentage so calculated agrees very closely with that which the analysis of the entire wheat-grain or its ash would indicate. Thus we may mention, that according to the sum of the phosphoric acid distributed in the different products, we have 50·7 per cent. of it in the ash of 100 of grain or meal; whilst the average percentage obtained in the analyses of the six ashes of the produce of the same season, was 49·8, an approximation sufficiently near to give some confidence, at least in the relative accuracy of the numerous analytical results involved in such an estimate.

Before leaving the question of the comparative chemical composition of the different products obtained by means of mechanical separation from wheat-grain, attention may be called to some results of this kind, in connection with the products of the Colonial steel-hand-mill, which was first employed in these experiments. As will be seen, the results now to be recorded agree in general tendency with those already given; yet they have some special and curious points of interest. The individual nitrogen determinations are given in Table XI, and the collected results of the examination of the various products in Table XII.

TABLE XI.

Nitrogen per Cent. in the Products of Wheat-Grain, from the
Colonial Steel-hand-mill.

(In natural State of Dryness.)

| Products from | Wheat-Grain, Harvest 1846. | | | | | |
|--------------------|----------------------------|------|-------|--------------|------|-------|
| | Unmanured. | | | Manured. | | |
| | Experiments. | | Mean. | Experiments. | | Mean. |
| | 1. | 2. | | 1. | 2. | |
| First Grinding :— | | | | | | |
| Wire 1 | 1·94 | 1·89 | 1·91 | 1·59 | 1·60 | 1·59 |
| Wire 2 | 1·57 | 1·59 | 1·58 | 1·44 | 1·49 | 1·47 |
| Second Grinding :— | | | | | | |
| Wire 1 | 1·89 | 1·90 | 1·89 | 1·60 | 1·61 | 1·60 |
| Wire 2 | 1·73 | 1·78 | 1·76 | 1·53 | 1·65 | 1·59 |
| Wire 3 | 1·78 | 1·76 | 1·77 | 1·58 | 1·49 | 1·54 |
| Bran | 2·07 | 2·09 | 2·08 | 1·69 | 1·79 | 1·74 |

TABLE XII.

Composition of the Products of Wheat-Grain from the Colonial Steel-hand-mill.

| Products from | | Wheat-Grain, Harvest 1846. | | | | | | | | | |
|-------------------|----|-----------------------------|-----------------------|-----------|---------------------|-----------|-----------------------------|-----------------------|-----------|-----------------------------|----------|
| | | Unmanured. | | | | | Manured. | | | | |
| | | In 100 of each Product. | | | In 100 of each Ash. | | In 100 of each Product. | | | Mean of 5. | |
| | | Dry Substance (at 212° F.). | Mineral Matter (Ash). | Nitrogen. | Phosphoric Acid. | Magnesia. | Dry Substance (at 212° F.). | Mineral Matter (Ash). | Nitrogen. | Ash in 100 of each Product. | Product. |
| First Grinding.— | | | | | | | | | | | |
| Wire 1 .. | .. | 84.0 | 0.78 | 1.91 | 45.3 | 6.95 | 84.4 | 0.78 | 1.59 | 0.75 | |
| Wire 2 .. | .. | 85.2 | 0.77 | 1.58 | 45.0 | 6.25 | 83.9 | 0.79 | 1.47 | 0.78 | |
| Second Grinding:— | | | | | | | | | | | |
| Wire 1 .. | .. | 85.0 | 1.23 | 1.89 | 49.7 | 9.04 | 84.8 | 1.02 | 1.60 | 1.22 | |
| Wire 2 .. | .. | 85.0 | 1.17 | 1.76 | 52.0 | 9.09 | 85.3 | 1.07 | 1.59 | 1.24 | |
| Wire 3 .. | .. | 85.4 | 1.83 | 1.77 | 51.4 | 11.20 | 85.4 | 1.70 | 1.54 | 2.01 | |
| Bran .. | .. | 86.5 | 5.76 | 2.08 | 53.0 | 13.57 | 87.3 | 5.64 | 1.75 | 5.70 | |

It should be mentioned, in reference to the working of the steel-hand-mill, that on passing the grain through the apparatus, four products were first obtained, namely, two fine flours, thirds, and bran; the last two products of the first grinding being mixed together, were passed through the mill a second time, and four products again separated. After this explanation, the designation of the products in Tables XI and XII will be sufficiently intelligible.

With the information derived from the previously recorded results, a glance at the percentages of ash in the several products of the different grains, as given in Table XII, will show that the so-called "bran" here obtained, retained more flour than from the ordinary flour-mill. In fact it was obviously pretty nearly equivalent to the 9th, 8th, 7th, 6th, and part of the 5th products of the ordinary mill taken together. The five flours, on the other hand, but especially the three from the second grinding, obviously contained rather more branny particles than the ordinary bread-flours of the other series of the experiments. Such, indeed, was the obvious character from an inspection of the various products.

Consistently with the character of the products thus defined, the variations in their percentages of nitrogen are, upon the whole, much less than in the former series; but such as they are they are very curious. Thus in both instances, though in a less marked degree in the manured than in the unmanured specimens, the first product of the first grinding, gives a higher percentage of nitrogen than the second; that of the latter being in both cases exceedingly low. In the products of the second grinding, the tendencies are again parallel in the two series. Here again the first product gives a higher percentage of nitrogen than the second. The third is about equal to the second; and the fourth, or bran, is in both series the highest of the six products in this respect. Following up these curious results, which show that the mechanical means employed had the tendency, even within the limits of the farinal part of the grain, to separate products of different chemical characters—we may observe, that the fluctuation in the percentages of *ash*, are in detail strongly confirmatory of the direction of the variations in the amounts of nitrogen. Thus, whether we look to the average percentages of nitrogen and of mineral matter respectively, as influenced by season, and as illustrated in the Summary Table No. I—or to the parallel amounts in the several mill-pro-

ducts as shown in Table X, we see that with a rise in the percentage of nitrogen there is, in comparable cases, one in that of the mineral matter, and *vice versâ*. If with this point in view, and carefully considering the degree of these changes as shown in our more detailed Tables, we compare together the columns of nitrogen and of ash, we find that the fluctuation in the latter as seen in Table XII, are perfectly consistent in direction with those in the former. This is more particularly observable in the products of the unmanured specimen.

The middle Division of Table XII, shows as before, a rise in the percentage of the *phosphoric acid* in the ash, as we proceed from the finer to the coarser products. The *magnesia*, too, follows the same order, the ash of the "*bran*" containing about twice as much as that of the flours of the first grinding.

In the last column of the Table XII, for the sake of comparison with the individual results in the former ones, we have the mean percentage of mineral matter for each product, of five lots of grain which were similarly experimented upon in the steel-hand-mill.

The next step in the prosecution of our inquiry would obviously have been—to separate the different proximate organic compounds, of some series of these grains and their various mill-products—to determine the amount and composition of the mineral matters associated with each—and to submit the different grains, and their mechanically separated parts, to microscopic examination. Had this been accomplished, the results would probably have been of high interest to the vegetable physiologist; and they would probably have tended to throw some light on the functional actions or special offices, of the different mineral constituents known to be essential to the growth and elaboration of vegetable products. This labour, however, from pressure of other investigations, we have hitherto been obliged to forego; though several series of the mill-products themselves (necessarily to a certain degree artificially dried), and also of their respective ashes, have been preserved with a view to the prosecution of the subject, either by ourselves or others, at some future time, as far as such specimens will allow.

A great many scientific observers have investigated the questions—of the practical yield of bread-flour from 100 of grain or meal—of the produce of bread from 100 of flour—of the amounts

of dry substance, of water, and of nitrogenous compounds, in bread—and of the changes which the flour undergoes in the bread-making process. The question as to what are the chemical qualities upon which depend the practical estimate of the miller and the baker, of the comparative values of different flours for the purposes of bread-making, has also frequently been discussed; the conclusion generally arrived at being, that it is the percentage amount of nitrogen or of gluten which rules this practical estimate. The opinion that the comparative value to the *consumer*, too, is measurable by the same standard as to chemical composition, is also pretty universal. With regard to the latter points we may at once observe, that the tendency of more recent investigations is, at least to modify, the currently adopted views. That this was desirable, the whole course of our experimental inquiry and observation, during the last twelve years, has led us to believe; and we have occasionally treated of the subject in some of its aspects elsewhere.

Without hoping to settle dogmatically, questions involving too many factors to be dealt with in such a manner, we propose now to adduce some few experiments and arguments of our own, which may have a bearing upon some of those above enumerated; and we shall also provide as summary a view as possible, in a tabular form, of such published results of others, on some of the points capable of illustration in that way.

In the following Table XIII, are given:—

- 1st. The results of some experiments of our own, on the amount of bread yielded by 100 of the flour taken from the different parts of the dressing-machine; in some cases using the products of each of the first 4 wires separately, and in others (19 in number), taking the products 1, 2, and 3, mixed together.
- 2ndly. The determinations (at 212° F.) of the dry substance, and of water, in Country, and in London bakers' loaves.
- 3rdly. The recorded results of others, on—the yield of flour from 100 of grain—the yield of bread from 100 of flour—and on the percentages of dry substance, and of water, in bread.

Recorded Observations—*continued*.

| | | | | | Flour from 100 Grain. | Bread from 100 Flour. | In 100 Bread. | |
|------------------------------|----|------|----|----|-----------------------------|-----------------------------|---------------------|--------|
| | | | | | | | Dry Sub- stance. | Water. |
| JOHNSTON— | | | | | | | | |
| English | .. | .. | .. | .. | 75·7 | 150·0 | 56·0 | 44·0 |
| English and French Ration .. | .. | .. | .. | .. | .. | .. | 49·0 | 51·0 |
| BOUSSINGAULT— | | | | | | | | |
| English | .. | .. | .. | .. | 72·0 | | | |
| French | .. | .. | .. | .. | 74·0 | | | |
| Paris | .. | .. | .. | .. | .. | 130·0 | 64·6 | 35·4 |
| Bechelbronn | .. | .. | .. | .. | .. | 140·0 | 57·1 | 42·9 |
| French Ration | .. | .. | .. | .. | .. | 139·0 | | |
| Syrington | .. | .. | .. | .. | 78·0 | | | |
| Lurzer | .. | .. | .. | .. | 83·0 | | | |
| Dombasle | .. | .. | .. | .. | 85·5 | | | |
| PELIGOT | | | | | 80·0 | | | |
| PAYEN— | | | | | | | | |
| Paris, Ordinary | .. | .. | .. | .. | .. | .. | 64·0 | 36·0 |
| " French " | .. | .. | .. | .. | .. | .. | 62·0 | 38·0 |
| French Ration | .. | .. | .. | .. | 85·0 | .. | 61·0 | 39·0 |
| " " " " | .. | .. | .. | .. | 80·0 | .. | 58·0 | 42·0 |
| English Cubic Loaf | .. | .. | .. | .. | .. | .. | 60·0 | 40·0 |
| " " " " | .. | .. | .. | .. | .. | .. | 52·0 | 48·0 |
| | | | | | Caled. | Expt. | | |
| MILLON— | | | | | | | | |
| 1. | .. | .. | .. | .. | 136·0 | 135·0 | 65·0 | 34·98 |
| 2. | .. | .. | .. | .. | 137·0 | 137·0 | 63·4 | 36·6 |
| 3. | .. | .. | .. | .. | 131·5 | 132·0 | 63·5 | 36·5 |
| 4. | .. | .. | .. | .. | 136·0 | 134·5 | 61·3 | 38·7 |
| 5. | .. | .. | .. | .. | 133·0 | 133·0 | 63·3 | 36·7 |
| 6. | .. | .. | .. | .. | 134·5 | 133·0 | 65·5 | 34·5 |
| 7. | .. | .. | .. | .. | 135·0 | 134·0 | 66·0 | 34·0 |
| 8. | .. | .. | .. | .. | 137·0 | 137·0 | 64·9 | 35·1 |
| 9. | .. | .. | .. | .. | 133·0 | 134·0 | 60·5 | 39·5 |
| Mean | .. | .. | .. | .. | 134·8 | 134·4 | 63·7 | 36·3 |
| Military | .. | .. | .. | .. | .. | .. | 58·0 | 42·0 |
| " " " " | .. | .. | .. | .. | .. | .. | 57·0 | 43·0 |
| | | | | | Nit. Mat. | | | |
| MACLAGAN— | | | | | | | | |
| Bakers' First Quality .. | .. | 7·55 | .. | .. | .. | 134·7 | 64·25 | 35·75 |
| " Second " | .. | 7·99 | .. | .. | .. | .. | 65·09 | 34·91 |
| Home-baked, First Quality .. | .. | 7·29 | .. | .. | .. | 131·0 | 66·1 | 33·9 |
| " Second " | .. | 8·71 | .. | .. | .. | 133·0 | 58·3 | 41·7 |
| Unfermented, First " .. | .. | 7·00 | .. | .. | .. | 143·0 | 60·5 | 39·5 |
| " Second " | .. | 7·40 | .. | .. | .. | .. | 58·5 | 41·5 |

Setting aside the incidental but much accounted measure of the quality of flour—colour, it may be said, that the standard of excellence of the baker, is founded on the weight of the loaf, which, consistently with proper texture and lightness, can be obtained from a given weight of flour. Leaving for the present the discussion of the question upon what point or points of chemical composition, these properties individually or collectively depend, we may observe, that so far as our own experiments on the small scale go, the quality of yielding the greatest *weight* of bread from a given amount of flour, certainly did not seem to attach to the highest separated product of the dressing-machine; which, according to the results recorded in Table X, would probably contain slightly the smallest proportion of nitrogen, and consequently the largest amount of the starch series of compounds. On the other hand, looking at the results more in detail than they are given in the Table, it appears that the products of the grain of 1846 gave a notably greater weight of bread than the corresponding products of the more highly nitrogenous grain of 1847—the grain of the former year, being admittedly a somewhat fuller and better sample than that of the latter. Judging then between the different products of the same grain, the experiments showed the weight of bread from a given weight of flour to be greater as we proceed from the less to the more nitrogenous products, so long as the comparison is made between the first three or fine flours only. The fourth product, however, containing still more nitrogen, but probably in a different condition, gave a less proportional weight of bread, notwithstanding that it also contained a considerable amount of branny particles, which it has been stated, have the property of retaining water by virtue of their structure independently of mere chemical composition. Comparing year with year on the other hand, the separate products of the grain of highest weight per bushel, of lower nitrogen, and admittedly of the best development, afforded the largest produce of bread.

Passing from the experiments on the individual products to those on the mixture of the first three of them, which would together constitute a *fine* bread-flour, we see that with this combination there was, on the average, a higher yield of bread than from either of the separate products. This was not the case taking the flours of 1846 alone; but it was remarkably so with those of 1847, the season of rather higher percentage of nitrogen; and it should be added, that whilst on the average the mixed products of

1846 represented only 68·3 per cent. of the entire grain, those of 1847 represented 71·5 per cent. Although, however, there is thus observed a tendency to increase in the *weight* of bread, the higher the percentage of nitrogen within the range of the finer flours, and especially so when mixed, yet the grains and the flours of 1846, were pronounced by an experienced miller, to be superior to those of 1847, and they would doubtless have given, on the large scale, a loaf of whiter, lighter, and better texture.

In all these trials exactly the same treatment was adopted, but as the result may be different in operating upon small and large bulks respectively, the method followed should be described. 32 ounces of flour were taken, and given weighed quantities of compressed yeast, and of salt, were always employed. Water of a uniform temperature was also used, and was worked in by a practised hand, until the dough was decided to be of the proper consistency. The weight of water taken up, was then determined. The dough was always made quite late in the evening, and after being allowed to ferment during the night, it was put into a baker's oven early the following morning. Finally, the loaves were weighed hot from the oven, and again when quite cold, towards evening. From the second weight, the increase upon the original weight of flour was ascertained; and, the percentage of dry substance in the flours being previously known, the percentages of dry matter and water in the bread were calculated, making no allowance, however, for the probably $\frac{1}{2}$ per cent. of dry substance lost by fermentation. The experiments of Millon given in the lower part of the Table XIII, as well as the conclusion of other recent experimenters, indeed seem fully to justify the assumption, that the loss from that cause perhaps need not be estimated at more than the small amount above supposed.

For the sake of comparison, and as a check to our own bread-making experiments, and calculations thereupon, three loaves were bought at random, at as many different bakers in the city of London, and four from as many in our own locality in the country; and upon half of each of these, first finely divided, the dry substance was determined in a water-bath at 212° F. It will be seen, that the mean of our own experiments with the separate products, gives, by calculation as above alluded to, 62·8 per cent. dry substance, and 37·1 water, in the bread; and that with the products 1, 2, and 3 mixed, gave 61·4 dry matter, and 38·6 water.

The four country bakers' loaves (in July 1856—probably from wheat of 1855), gave 62·1 dry, and 37·9 water; and the three London ones 64·2 dry, and 35·8 water. It is thus seen, that our own results from the various flours of grain from two different harvests, agree very closely with those of the country bakers' bread from a third. They, together, indicate an average of 37 to 38 per cent. of water in the bread. The London bakers' loaves, which, however, had probably been four hours longer out of the oven than the country ones, gave 64·2 of dry = 35·8 of water. Upon the whole, then, these experiments, from the flours of three different seasons, indicate a probable average range of from 36 to 38 per cent. of water in bread; and, taking an average of 15 per cent. water in flour, and assuming the loss of dry matter by fermentation, and the gain by fixed saline matter added, to about neutralize each other, this would be equivalent to, from 132·8 to 137·1 parts bread for 100 of flour.

A reference to the recorded results of others, as given in the Table (XIII), will show that this average of 36 to 38 per cent. of water in bread, agrees very closely with the estimate of Dumas; with that of Payen, for the ordinary bread of Paris; with that of Boussingault, for Paris bread; with the mean of four kinds of fermented bread experimented upon by Dr. MacLagan; with that of nine by Millon; and with the estimate of Alison and Christison. The estimate by Payen, of 40 to 48 per cent. of water in the English cubic loaf, is undoubtedly too high for English bakers' bread as usually sold. The estimates by Johnston, of 44 per cent. water in English bread, and of 51 per cent. in English and French ration-bread, are also, no doubt, too high. The results of Boussingault in France agree with our own in England, in showing country bread to contain, usually, more water than that of the cities. Ration-bread seems, according to most observers, to be moister than that in ordinary use. To conclude on this point, although it is very desirable to have a proper estimate of the probable average proportion of dry substance contained in the most important article of the food of our population, yet it is obvious that many circumstances must influence the amount in individual cases. The length of time that the bread has been withdrawn from the oven, must of course be taken into account; but in fixing general averages, perhaps it is better to take it within the first twelve hours, as this will best represent the weights as

delivered by the baker, and, consequently, those estimated as consumed.* It must be remembered, too, that the character of the ripening season greatly affects the quality of the flour, and in giving from the results of others as well as of ourselves, a probable average of 36 to 38 per cent. water, or 62 to 64 per cent. of dry substance in bread, we would at the same time remark, that all our own special data, are derived from experiments on the produce of three seasons of higher than average maturing character.

That the *season*, independently of either soil or manuring, may very much influence the percentage of nitrogen in one and the same description of grain, even in the same locality, is amply illustrated by the results in Tables I and III, given at the commencement of this paper. It cannot be wondered at, therefore, that different localities or countries, should yield us grains showing a wide range of variation in their percentages of nitrogenous compounds. Rossignean, Boussingault, Millon, and Peligot have examined many of the characteristic wheats of commerce, and we propose here to subjoin some additional facts relating to this branch of the subject.

In the following Table (XIV) are given the mean results of a great many determinations, by the mechanical method, of the *gluten* in flour, by Mr. W. Constable, of Brighton. It is admitted that this method is an uncertain one, and it is, of course, quite incompetent to indicate the *total nitrogenous* substance of the flours. However, we believe the experiments to have been made with great care and uniformity of manipulation, and, as they are also consistent with results of another kind, they are well deserving record. It may be premised that, whilst the method in question is liable to a little depreciation in the amount of gluten by loss in the washing—especially when the substance itself is of an inferior character—yet, on the other hand, the drying is more likely to be in error in the other direction. These two sources of error, therefore, so far as they operated in the experiments, would tend to neutralize each other. It may be added, that not the least interesting part of Mr. Constable's results, is that he, consistently with the observations of Peligot and others, establishes a very wide range in the *character* of the gluten obtained from different flours,

* It should be stated, however, that, if the fresh weight of the 7 baker's loaves examined were assumed to be 4 lbs. each, as it should have been, then the dry matter which the loaves contained was, on the average, only equal to $60\frac{1}{2}$ per cent; the water, on the same calculation, being, of course, $39\frac{1}{2}$ per cent. !

as to colour, tenacity, elasticity, and so on. Mr. Constable's results, with which he has kindly furnished us, are recorded by him seriatim, in the order in which they were obtained, and without any special reference to the point for the illustration of which we here adduce them. It will be seen that in our Table, we have classified the results according to their reputed locality of growth or shipment, and arranged the *means* so obtained somewhat in the order of latitude, ranging from north to south, adopting the same general arrangement for the European and American samples respectively.

TABLE XIV.

Percentage of Gluten in different Flours.

MEAN RESULTS.

| Reputed Localities of Growth or Shipment. | | | | | Number of Experiments. | Mean Gluten Per Cent. |
|---|----|----|----|----|------------------------------|-----------------------------|
| America— | | | | | | |
| Canada | .. | .. | .. | .. | 6 | 9·8 |
| Genessee (New York) | .. | .. | .. | .. | 7 | 9·8 |
| Other New York | .. | .. | .. | .. | 7 | 10·1 |
| Ohio | .. | .. | .. | .. | 18 | 11·8 |
| Maryland | .. | .. | .. | .. | 3 | 11·3 |
| Richmond (Virginia) | .. | .. | .. | .. | 8 | 11·8 |
| George Town (South Carolina) | .. | .. | .. | .. | 18 | 13·7 |
| New Orleans | .. | .. | .. | .. | 1 | 13·4 |
| Miscellaneous | .. | .. | .. | .. | 11 | 9·35 |
| Mean .. | .. | .. | .. | .. | 79 | 11·4 |
| North Europe— | | | | | | |
| Dantzic | .. | .. | .. | .. | 4 | 8·9 |
| Hamburg | .. | .. | .. | .. | } | 10·3 |
| Stettin | .. | .. | .. | .. | | |
| Pomerania | .. | .. | .. | .. | | |
| South and East Europe— | | | | | | |
| Tuscany | .. | .. | .. | .. | } | 10·3 |
| Spain | .. | .. | .. | .. | | |
| Portugal | .. | .. | .. | .. | | |
| Black Sea, Soft | .. | .. | .. | .. | 2 | 12·5 |
| Black Sea, Hard | .. | .. | .. | .. | 9 | 14·9 |
| Mean .. | .. | .. | .. | .. | 31 | 11·6 |
| England— | | | | | | |
| White | .. | .. | .. | .. | 45 | 10·8 |
| Red | .. | .. | .. | .. | 13 | 10·4 |
| Not Specified | .. | .. | .. | .. | 45 | 10·5 |
| Mean .. | .. | .. | .. | .. | 103 | 10·7 |

It cannot fail to be observed, that there is a general tendency in the specimens from both the European and American continents, to increase in the percentage of gluten, proceeding from the north to the south. It may therefore be concluded that, among other circumstances, a relatively high temperature at the ripening period is favourable to a high per-centage of gluten. The mutual adaptations of heat and moisture, throughout the various stages of the progress of the plant, are, however, so almost infinitely varying, even from season to season, in one and the same locality, that it is not surprising there should be many exceptions to any such sweeping generalization as the one here indicated, in regard to widely differing localities. A study of the variations in the character of the crop, and in the composition of the grain grown from year to year in our experimental field, side by side with the varying circumstances of root and leaf supply of moisture, and of temperature, is sufficient to show how numerous, and how indeed ever changing in their mutual relations, are the factors which lead to one or another order of development in the growing plant.

We have at various times determined the nitrogen in individual specimens of foreign wheat which have come in our way, and recently, through the kindness of Mr. W. J. Harris, of Fenchurch Street, London, we have been provided with a series of characteristic samples, the result of the examination of which we had hoped to embody in this paper. Unfortunately, the laboratory work is not sufficiently completed to allow of this, any further than by a few general remarks on the tendency of the results already obtained. This tendency, from the examination of a series of contrasted samples, is fully to confirm the indications of Mr. Constable's results as to general influence of latitude, or locality, on the nitrogenous percentage of the grains. There are, however, as above inferred, some interesting and instructive exceptions brought to light. It is obvious, too, that both soil and variety, must have much to do with the character of the grain; and that to elicit without exception, the influence due to climate alone, the same description of wheat should be grown in as far as possible similar soils, in different localities, for a series of years consecutively. In defect of specimens of this kind, we must to a certain extent rely on the assumption, that those descriptions will be generally cultivated in a particular locality, which experience has shown to be most adapted to its climate and other characters, and that hence the qualities of the

grains, will be at least some indication of the general tendencies of the climatic circumstances which have yielded them.

It may be remarked, that among the American specimens examined by Mr. Constable, the Genessee is seen to contain the lowest average percentage of gluten, yet it is one of the most highly esteemed of the American flours imported into this country. Again, among the foreign European samples enumerated, the Dantzic yielded the smallest percentage of gluten, whilst it has above all the highest range of value in the English market. The soft Spanish is perhaps the next in order of value among the imported European wheats, and we may observe that it is also one of the lowest in percentage of nitrogen which we have yet examined. On the other hand, the flours from many of the *highly* nitrogenous foreign wheats, have the undoubted character of imparting great "*strength*" to the dough, and for this purpose, they are much valued to *mix* with weaker flour; especially with that from grain which has been imperfectly developed and matured. Some of the most important of these highly nitrogenous wheats are, however, both inferior in the colour of their flour, and very hard and horny; and owing to the inappropriateness of the English method of milling, to the defective whiteness of the flour, and of the bread, and to the somewhat close texture of the latter, other flours of lower percentages of nitrogenous compounds have, notwithstanding this great "*strength*," a higher character when used alone for bread-making purposes. These highly nitrogenous wheats are chiefly imported from Russia, and independently of a high ripening temperature, they are for the most part grown on very rich soil, and sown in the Spring. On this point it is worthy of notice, that home-grown Spring wheat, has sometimes the character of imparting strength to the flour of an inferior Winter wheat, and in the only instance of this kind which we have examined, the reputed stronger (Spring) wheat, had the higher percentage of nitrogen.

It may be stated generally, that the highly nitrogenous foreign wheats, have the admitted character of imparting strength to inferior flour; and they are thus highly valued for the purpose of admixture with home-grown grain imperfectly developed and matured. These highly nitrogenous imported wheats have, as the rule, been matured under a much higher temperature than our own; their nitrogenous constituents would appear to be in larger proportion in the form of gluten; and it is in wheats so ripened,

that the higher percentage of fatty matter is also found, the proper blending of which, according to the experiments of Peligot, considerably affects the physical characters of the gluten. The opinion of Peligot—indeed of other recent investigators, and in this we fully concur—is, that the measure of value of different flours for the purposes of bread-making, is certainly much more dependent on the *condition* of their constituents, than on their mere percentage amount of nitrogenous compounds. This high *condition* of the nitrogenous, and also the other compounds, would seem to be alike possible in wheats of high and of somewhat low percentage of nitrogen—provided, other things being equal, they have been well developed, and ripened at a high temperature; whilst, when this is so, an undoubted preference is given to the less nitrogenous grains. This is partly due to the latter being generally softer, and more amenable to current milling methods; and partly to the widely-differing structural character of the farinal matter, by virtue of which the flour not only makes a better and more workable dough, but the bread produced is of superior texture and lightness—conditions which all analogy would lead us to conclude, must materially aid its digestion and assimilation, and consequently so far increase its value as food.

A high percentage of nitrogenous compounds, provided the grain be well-developed and matured, and not so hard as to offer mechanical obstacles to fine division and easy separation of the bran in the mill, will tend to a great weight of bread, and a good quality as to texture. It would appear, however, that a smaller percentage, if with equally high elaboration, will tend to a similar result as to weight, and to even higher qualities as to texture and whiteness. Within the limits of our own island, however, on the average of seasons, the better-elaborated grain will probably be the less nitrogenous,* though the nitrogenous matter it does contain, will be in a high condition as to elaboration, and to its mutual relations, structural and chemical, with the other constituents of the flour. Hence it comes to pass that, as our home-grown flours go, those which are the best in the view of the baker, will frequently be those having a low *percentage* of nitrogenous compounds—a higher *condition* more than compensating for the

* This is, however, not always the case; and, had we extended our review beyond the ten years to which Tables I and III refer, we should have found, in the season of 1855, both high development and maturation of grain, and high percentage of nitrogenous compounds. Of the cases included in our survey, the season of 1847, afforded in the highest degree the combination of characters here referred to.

higher percentage of nitrogen, generally associated as it is in our climate, with an inferior degree of development and maturation.

We conclude, then, that condition of *maturation*, or perhaps rather *elaboration*, as well as mere percentage composition, should be theoretically, as it is practically, admitted as an essential element in estimating the relative qualities of different wheats or flours, for bread-making purposes. The opinions of some of the most recent, and perhaps the most competent observers, certainly point in the same direction as the one here indicated. Still, the current opinion derived from several of our standard works, would seem to be, that a high percentage of nitrogenous compounds should be taken as an almost unconditional measure of value.

But besides the frequently reiterated statement that the baker's estimate is founded on the amount of the gluten, it is also pretty generally maintained, that it is the amount of this, or of the nitrogenous constituents collectively, which determines the comparative values of different flours or breads, to the *consumer*. With regard to those foreign wheats which have their nitrogenous substance in a highly-elaborated condition, and favourably related to the other matters, and in which the whole is structurally fitted for easy milling, and to yield a light and easily-digestible bread, we would not say that, with such, a comparatively high *percentage* also of the nitrogen, might not be an additional point of value. But, even with the foreign wheats, it is but a small proportion that combine these several qualities; whilst those which have the most of the others, have, generally, less of the *amount* of nitrogenous substance. With home-grown wheats, too, as already said, information at present at command tends to show, that high percentage of nitrogen is, frequently at least, associated with *low condition of elaboration* of the constituents of the grain, yielding an inferior bread-flour—and thus, though from opposite causes to those which depreciate the richer nitrogenous grains of the higher-ripening temperatures, a less valuable food.

Let it be conceded, then, that condition, or elaboration, must affect the digestibility and assimilability of our food. But, we think it may be inferred, yet on other grounds, *that, as flours go*, the richer in the more directly respirable and fat-forming compounds, will generally be more valued as food.* The following Table (for

* There is experimental evidence to show, that the nitrogenous constituents of food may serve one or both of these offices; but, when in excess, probably at a greater cost to the system.

some of the data of which we are indebted to Dr. Playfair), showing the estimated average percentage of nitrogen and of carbon in a number of standard articles of food, and also the relation in them of the one constituent to the other, will aid us in illustrating our meaning :—

TABLE XV.

Estimated Average Composition of Standard Articles of Food.

| Foods. | Per Cent. | | | Nitrogen to 100 Carbon. |
|--------------------------------------|-------------------|---------|-----------|-------------------------------|
| | Dry Substance. | Carbon. | Nitrogen. | |
| Meat (fresh) | 45·0 | 30·0 | 2·0 | 6·6 |
| Bacon (green) | 80·0 | 57·0 | 1·13 | 2·0 |
| „ (dried) | 85·0 | 61·0 | 1·4 | 2·3 |
| Suet or Butter | 85·0 | 68·0 | 0·0 | |
| Milk | 10·0 | 5·4 | 0·5 | 9·3 |
| Cheese | 60·0 | 36·0 | 4·5 | 12·5 |
| Flour (wheaten) | 85·0 | 38·0 | 1·72 | 4·5 |
| Bread | 64·0 | 28·5 | 1·29 | 4·5 |
| Maize | 87·0 | 40·0 | 1·75 | 4·4 |
| Oatmeal | 85·0 | 40·0 | 2·0* | 5·0 |
| Rice | 87·0 | 39·0 | 1·0 | 2·56 |
| Potatoes | 25·0 | 11·0 | 0·35 | 3·2 |
| Vegetables (succulent average) | 15·0 | 6·0 | 0·2 | 3·3 |
| Peas | 85·0 | 39·0 | 3·65 | 9·4 |
| Sugar | 95·0 | 40·0 | 0·0 | |
| Cocoa and Chocolate | 92·0 | 56·2 | 2·0 | 3·6 |
| Beer or Porter | 9·5 | 4·5 | 0·01 | 0·2 |

By this Table it is seen, that wheaten flour and bread contain as high a proportion of nitrogen to carbon as most of the current articles of food of our working population, excepting the important items of fresh meat, milk, and cheese. Were we to ask, to what staple articles the working man next resorts, when his means allow him to add other foods to his main diet of bread?—the answer would be, cheese, bacon, and, perhaps, butter; and we think it would further be, that his preference would generally be for the bacon. The Table shows that, so far as he took cheese, he would considerably increase the proportion of the nitrogen to the carbon he so consumed. The amount of it he would eat would, however, be less than that of bacon, and in the latter he would only consume half as much nitrogen, in proportion to the carbon, as he would in bread alone. In fat, or butter, he would have no nitrogen

* Scotch oatmeal would range higher than this.

at all, so that the addition of either of these to his flour or bread, would still further reduce the proportion of nitrogen to carbon in his food. But all these substances, besides their respirable carbon, have a large proportion of respirable hydrogen, due to their *fatty substance*. Even cheese, which contains the least amount of this, has, nevertheless, a very considerable percentage of it; bacon much more; whilst fat and butter, excluding their water, are, of course, wholly composed of it. If, therefore, we take into calculation the respirable hydrogen, it will be seen that the *respiratory capacity* (so to speak) of the cheese, would be much higher relatively to the *flesh forming*, than the relation to the carbon alone, as in the Table, would indicate. In the bacon, on the other hand, the relation even of the carbon alone to the nitrogen, is much greater than in bread; and, if we further take into account its respirable hydrogen, its respiratory, relatively to its flesh-forming capacity, will appear still greater in comparison with the bread. Lastly, even taking the case of fresh meat, so large is its amount of fat, and, therefore, of respirable hydrogen, that its respiratory and fat-forming, relatively to its flesh-forming capacity, would be much higher, as compared with bread, than the figures in the Table, relating to carbon alone, would show.

From these considerations we think it may fairly be concluded, that the first more urgent call of the system of our under-fed, or only bread-fed, working man, is for an increased supply of respiratory or fat-forming, rather than of flesh-forming, constituents of food. Indeed it is to *fat itself*, in some form, that he first resorts.

If, then, the first demand of the system be generally for more of the more directly respirable or fat-forming material, than bread alone supplies:—if the foreign wheats of more than average percentage of nitrogen have, frequently, structural characters which render them with greater difficulty made into an easily-digestible bread:—if the more highly-nitrogenous wheats of our colder summers have their constituents frequently in a less highly-elaborated condition:—and if, finally, the introduction of more of the nitrogenous constituents of our grain into the bread-flour, generally introduces at the same time branny particles which cause the food to pass in too large a proportion undigested from the body—it would appear, that the standard of value of food-stuffs as they go, according to their nitrogenous percentage, is, at least, only conditionally correct, and that the current views on the point require to be somewhat modified.

From all the data at our command we have adopted 1.29 as the probable average percentage of nitrogen in wheaten bread. That

taken by Dr. Maclagan is from 1.1 to 1.2; and that by Playfair and Payen about 1.1. These amounts represent respectively about 8, $7\frac{1}{2}$, and 7 of nitrogenous compounds.* It will not be supposed that, because, from the facts adduced, we are led to believe that, in addition to such a bread as is here assumed, the first call of the system of the working man would be for more of respiratory and fat-forming material, we would therefore deny the advantage of an increased supply of nitrogenous constituents also. We would, however, submit, as worthy of reflection, that, whilst the relation of nitrogen to 100 of carbon in wheaten flour and bread is 4.5, that in the average of the food consumed, taking eighty-six cases, divided into fifteen classes, and including both sexes and all ages, was only 5.34. These dietaries included many which were exceedingly liberal, so far as the nitrogen supplied was concerned; yet a careful consideration of their details showed that, taking into calculation their respirable hydrogen, the relation of purely respiratory, or fat-forming, to flesh-forming material, in most of these numerous dietaries, would be nearly as great in bread. Indeed, it would appear that, that which is admitted to be a superior class of diet, is distinguished much more by including a certain amount of the important non-nitrogenous constituents, in the condition, and state of concentration, as in fatty matter, and of the nitrogenous ones, in the high condition, as in animal food, than by the higher proportion of its flesh-forming to its more exclusively respiratory and fat-forming constituents.

II.—*On a new Series of Organo-Thionic Acids.*

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THE researches of Dr. Frankland† have shown that there exists a class of bodies containing metals in combination with the alcohol radicals, and to which he has given the name of “organo metallic bodies.” One of the peculiar features possessed by these compounds is, that they bear a very strong molecular analogy to the inorganic compounds of the metal they contain, which inorganic compounds may therefore be regarded as the types of their organic derivatives. Thus antimony, which with hydrogen, forms anti-moniuretted hydrogen SbH_3 , and with oxygen teroxide of antimony SbO_3 , gives with ethyl, stibethyl $\text{Sb}(\text{C}_4\text{H}_5)_3$; and arsenic which

* These estimates have reference to the bread from rather fine flour; that from the coarser flours contains rather more of nitrogenous matters.

† Chem. Soc. Qu. J. vi. 57, and Phil. Trans. 1852, p. 417.

with the inorganic elements, sulphur and hydrogen, gives arseniuretted hydrogen AsH_2 , and bisulphide of arsenic AsS_2 , forms with methyl, cacodyl $\text{As}(\text{C}_2\text{H}_3)_2$; and with ethyl, ethylic cacodyl $\text{As}(\text{C}_4\text{H}_5)_2$. Cacodyl also unites with oxygen, forming oxide of cacodyl $\text{As} \left\{ \begin{smallmatrix} (\text{C}_2\text{H}_3)_2 \\ \text{O} \end{smallmatrix} \right\}$ resembling arsenious acid AsO_3 ; and cacodylic acid, agreeing with arsenic acid. From the recent researches of Wöhler, Hofmann, and Cahours, it appears that this singularity of behaviour is not exclusively confined to the combinations of metals with the alcohol radicals, but that the metalloids selenium and phosphorus, form with these radicals, compounds molecularly similar to their inorganic types, and possessing for the most part the property of uniting directly with oxygen. Thus selenethyl forms with oxygen, oxide of selenethyl $\text{Se} \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O} \end{smallmatrix} \right\}$ which is molecularly homogeneous with selenious acid SeO_2 , whilst phosphorus with ethyl, gives phosphethyl $\text{P}(\text{C}_4\text{H}_5)_3$ corresponding with phosphorus acid PO_3 . Considering the strong analogy existing between sulphur and selenium, I was induced to try whether the sulphide of ethyl would not, like selen-ethyl, unite with oxygen to form compounds of the thionic acid type.

In preparing sulphide of ethyl for this purpose, I tried several of the methods usually recommended, but found most of them to yield only a very poor product. By passing chloride of ethyl into an alcoholic solution of protosulphide of potassium, I obtained only traces of the compound; and the distillation of dry protosulphide of potassium with sulphovinate of potash yielded scarcely a better result. The following method, however, gave a satisfactory product:—An alcoholic solution of protosulphide of potassium was made, by saturating a weighed quantity of caustic potash, dissolved in alcohol, with sulphuretted hydrogen, and adding to this the same weight of alkali as that previously used. This alcoholic solution of protosulphide of potassium, on distillation with sulphovinate of potash, yielded a large quantity of sulphide of ethyl.

The sulphide of ethyl thus prepared, was treated with dilute nitric acid. On the application of a gentle heat, dense nitrous fumes were given off, the sulphide of ethyl entirely disappearing. When all action had ceased, the liquid, which contained an excess of nitric acid, was evaporated for some time in a water bath to expel as much as possible of this acid; it was then saturated with carbonate of baryta, and the evaporation continued to dryness. The dried mass being afterwards treated with alcohol and filtered

from the nitrate of baryta, the filtrate on long exposure to the heat of a water-bath yielded a small quantity of a thick syrupy liquid, which contained sulphur, ethyl, and baryta, but showed no disposition to crystallize, and could not be obtained in a satisfactory state for analysis. This experiment showed, however, that an acid had been formed which most probably contained sulphur, ethyl, and oxygen; but finding that this acid was obtained in such small quantities from sulphide of ethyl, I abandoned this process of forming it.

The recent researches of Dr. Frankland on the substitution of oxygen by an alcohol-radical in the case of binoxide of nitrogen,* led me to hope, that a corresponding reaction with an oxygen compound of sulphur and one of the organo-zinc compounds, would produce the desired substitution.

For obvious reasons, I selected for this reaction sulphurous acid and zinc-ethyl; and a preliminary experiment showed, that these bodies act upon each other very energetically, forming a white crystalline mass, which was evidently the zinc-salt of a thionic acid. On a large scale the process was conducted as follows:—A quantity of zinc-ethyl, prepared according to the plan recommended by Dr. Frankland,† was placed in a flask, and sulphurous acid evolved from sulphuric acid and copper turnings, and dried by passing through a Woulfe's bottle containing concentrated sulphuric acid, was allowed to come in contact with it. The gas was very rapidly absorbed by the zinc-ethyl, and so much heat was produced, that it was found necessary carefully to cool the flask during the whole process of absorption. In a short time, a white crystalline body was formed in the zinc-ethyl, and gradually the whole contents of the flask were converted into a mass of minute crystals, which protected some of the zinc-ethyl from contact with the sulphurous acid; so that, unless the action of the gas was very prolonged, and the crystalline mass broken up, the latter effervesced with water, owing to the presence of undecomposed zinc-ethyl. After purification and crystallization, first from alcohol, and then from water, it yielded, on analysis, the following numbers:—

I. 6.02 grs., burnt with oxide of copper, a tube of peroxide of lead being interposed between the chloride of calcium tube and potash apparatus, gave 3.20 grs. of carbonic acid, and 1.91 grs. of water.

* Proceedings of the Royal Society, viii. 198. † Phil. Trans. 1855, p. 259.

II. 6.28 grs. similarly treated, gave 3.35 grs. of carbonic acid, and 2.16 grs. of water.

III. 6.155 grs. gave 3.25 grs. of carbonic acid, and 2.065 grs. of water.

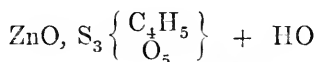
IV. 12.30 grs. dissolved in water and precipitated boiling by a solution of carbonate of soda, the precipitated basic carbonate of zinc washed, dried, and ignited, gave 2.995 grs. of oxide of zinc.

V. 5.96 grs. cautiously ignited, then treated with nitric acid, and afterwards strongly heated and exposed to a current of air, gave 1.46 grs. of oxide of zinc.

VI. 3.80 grs. ignited with a mixture of chlorate of potash and carbonate of magnesia, the product dissolved in hydrochloric acid and precipitated with chloride of barium, gave 7.82 grs. of sulphate of baryta.

VII. 3.14 grs. similarly treated, gave 6.67 grs. of sulphate of baryta.

These results, as is seen from the following comparison, agree with the formula :—



| Calculated. | | | | Analyses. | | | | | | | Mean. |
|-----------------|------------|-------|--|-----------|-------|-------|-------|-------|-------|-------|--------|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| C ₄ | . . . 24 | 14.41 | | 14.49 | 14.54 | 14.40 | — | — | — | — | 14.48 |
| H ₆ | . . . 6 | 3.60 | | 3.52 | 3.82 | 3.72 | — | — | — | — | 3.69 |
| Zn | . . . 32.5 | 19.52 | | — | — | — | 19.53 | 19.62 | — | — | 19.57 |
| S ₃ | . . . 48 | 28.82 | | — | — | — | — | — | 28.23 | 29.15 | 28.69 |
| O ₇ | . . . 56 | 33.65 | | — | — | — | — | — | — | — | 33.57 |
| 166.5 100.00 | | | | | | | | | | | 100.00 |

This compound is therefore the zinc-salt of a new acid, formed by the substitution of one equivalent of oxygen in three equivalents of sulphurous acid by ethyl. This acid I propose to call *Ethylotrithionic Acid*.

Ethylotrithionate of zinc presents the appearance of minute acicular crystals, which are colourless, and have a peculiar odour; they are almost insoluble in cold, but moderately soluble in boiling alcohol. It dissolves sparingly both in hot and cold water, and also in ether; on evaporating its aqueous solution, the salt crystallizes out as a pellicle which floats on the surface. Ethylotrithionate of zinc possesses a peculiar and somewhat bitter taste. It contains one atom of water of crystallization, which it retains at 100° C.

The crude salt produced by the action of zinc-ethyl on sulphurous acid, had not, however, such a simple constitution as the zinc-salt mentioned above, since, owing to the presence of an excess of oxide of zinc, derived from the action of water on the undecomposed zinc-ethyl, a basic salt had been formed. This salt submitted to analysis, yielded the following results:—

I. 5.42 grs. burnt with oxide of copper, yielded 2.47 grs. of carbonic acid, and 1.76 grs. of water.

II. 10.50 grs. dissolved in boiling water and precipitated with a solution of carbonate of soda, the precipitated basic carbonate of zinc washed, dried, and ignited, gave 3.305 grs. of oxide of zinc.

III. 4.63 grs. ignited with a mixture of chlorate of potash and carbonate of magnesia, the product dissolved in hydrochloric acid and precipitated with chloride of barium, yielded 8.37 grs. of sulphate of baryta.

The following calculation shows that these numbers agree with the formula:—

$$2(\text{ZnO},\text{S}_3 \left\{ \text{C}_4\text{H}_5 \right\}_{\text{O}_5} + \text{HO}) + \text{ZnO},\text{HO}$$

| Calculated. | | | | Analyses. | | |
|-----------------|---|---|-----------------------|-----------|-------|-------|
| | | | | 1 | 2 | 3 |
| C ₈ | . | . | 48 12.55 | 12.43 | — | — |
| H ₁₃ | . | . | 13 3.39 | 3.61 | — | — |
| Zn ₃ | . | . | 97.5 25.49 | — | 25.25 | — |
| S ₆ | . | . | 96 25.09 | — | — | 24.80 |
| O ₁₆ | . | . | 128 33.48 | — | — | — |
| | | | <hr/> 382.5 100.00 | | | |

Ethylotrithionate of Baryta, $\text{BaO},\text{S}_3 \left\{ \text{C}_4\text{H}_5 \right\}_{\text{O}_5} + \text{HO}$. — This salt is prepared by adding to a boiling solution of the zinc salt, caustic baryta in excess, and then passing carbonic acid through it till the excess of base is precipitated. It crystallizes on cooling from its concentrated solution in water, in the form of a pellicle, which floats on the surface. It is a colourless salt, which does not decompose when heated to 170° C; it contains one atom of water of crystallization, which is driven off at 100° C. Ethylotrithionate of baryta exposed for some time over sulphuric acid in vacuo, yielded the following analytical results.

I. 7.52 grs. burnt with a mixture of chromate of lead and oxide of copper, gave 3.34 grs. of carbonic acid, and 2.05 grs. of water.

II. 4.235 grs. dissolved in water, and the baryta precipitated with dilute sulphuric acid, gave 2.40 grs. of sulphate of baryta.

III. 6.35 grs. ignited with carbonate of magnesia and chlorate of potash, the product dissolved in hydrochloric acid, and precipitated with chloride of barium, gave 10.835 grs. of sulphate of baryta.

These results correspond closely with the above formula.

| Calculated. | | Analyses. | | |
|----------------|------|-----------|-------|-------|
| | | 1 | 2 | 3 |
| C ₄ | 24 | 12.11 | — | — |
| H ₆ | 6 | 3.03 | — | — |
| Ba | 68.6 | — | 33.33 | — |
| S ₃ | 48 | — | — | 23.11 |
| O ₇ | 56 | — | — | — |
| 202.6 | | 100.00 | | |

Ethylotrithionic Acid.— $\text{HO},\text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$ —To prepare this acid in its free state, a quantity of its zinc-salt was distilled with dilute sulphuric acid. The thermometer, during the distillation, stood fixedly at 140°C , and a liquid passed into the receiver which reddened litmus strongly, but contained the acid in a very dilute form. In the hope of obtaining it in a more concentrated state, the zinc-salt was distilled with strong sulphuric acid; but this method did not succeed, as the thionic acid was entirely decomposed, the mass in the retort being charred, and large quantities of sulphurous acid evolved, whilst an oily liquid with an alliaceous odour distilled over.

Finding, however, that neither of these methods was adapted for obtaining large quantities of the free acid, I exactly precipitated the baryta from ethylotrithionate of baryta, by dilute sulphuric acid, separated the sulphate of baryta by filtration, and thus obtained a moderately concentrated solution in water. A quantity of this aqueous solution was subjected to prolonged evaporation in a water bath, but the acid could not be obtained by this method in its monohydrated state; since, after very lengthened evaporation, it still retained five equivalents of water. To determine, however, whether the acid retained its original constitution, a baryta-salt was formed by dissolving in it a quantity of carbonate of baryta. The salt thus obtained, on being recrystallized from water and dried at 100°C , gave, on analysis, the following numbers, which

agree with the formula of the anhydrous baryta-salt of ethylo-trithionic acid :

I. 8.54 grs. burnt with chromate of lead, gave 3.79 grs. of carbonic acid and 1.825 grs. of water.

II. 4.47 grs. burnt with oxide of copper, gave 1.975 grs. of carbonic acid and 1.00 grs. of water.

III. 9.30 grs. dissolved in water and precipitated with dilute sulphuric acid, gave 5.44 grs. of sulphate of baryta.

IV. 4.43 grs. ignited with chlorate of potash and magnesia, the product dissolved in hydrochloric acid and precipitated with chloride of barium, gave 7.82 grs. of sulphate of baryta.

| Calculated. | | Analyses | | | | Mean. |
|------------------|-----------------|----------|-------|-------|-------|--------|
| | | 1 | 2 | 3 | 4 | |
| C ₄ . | 24 12.39 | 12.10 | 12.05 | — | — | 12.08 |
| H ₅ . | 5 2.58 | 2.37 | 2.18 | — | — | 2.43 |
| Ba . | 68.6 35.43 | — | — | 34.41 | — | 34.41 |
| S ₃ . | 48 24.79 | — | — | — | 24.22 | 24.22 |
| O ₆ . | 48 24.81 | — | — | — | — | 26.86 |
| | 193.6 100.00 | | | | | 100.00 |

Ethylo-trithionate of Silver.— $\text{AgO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$ —This salt was obtained by dissolving carbonate of silver in the free acid prepared as above. It is very stable, neither evaporation in a water-bath nor exposure to light decomposing it in the slightest degree. The ethylo-trithionate of silver is a white crystalline body very soluble in water; on exposure to the air, it rapidly attracts moisture, becoming liquid. It will bear heating to 100° C, but if the temperature be raised much above this, it is entirely decomposed. This salt after being dried over sulphuric acid in vacuo, yielded the following analytical results:—

I. 9.42 grs. burnt with oxide of copper, gave 3.52 grs. of carbonic acid and 1.882 grs. of water.

II. 8.30 grs. similarly treated, gave 3.15 grs. of carbonic acid and 1.66 grs. of water.

III. 10.75 grs. gave 4.005 grs. of carbonic acid and 2.17 grs. of water.

IV. 3.60 grs., cautiously ignited and exposed to a stream of air, gave 1.665 grs. of metallic silver.

V. 5.92 grs. similarly treated, gave 2.73 grs. of silver.

VI. 11.40 grs. dissolved in water and precipitated with hydrochloric acid, gave 6.995 grs. of chloride of silver.

VII. 5.27 grs. ignited with a mixture of chlorate of potash and carbonate of magnesia, the product dissolved in hydrochloric acid and precipitated with chloride of barium, gave 7.87 grs. of sulphate of baryta.

The following comparison shows that these numbers agree with the above formula :—

| Calculated. | | | Analyses. | | | | | | | Mean |
|----------------|-------|--------|-----------|-------|-------|-------|-------|-------|-------|--------|
| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| C ₄ | . 24 | 10.30 | 10.20 | 10.35 | 10.16 | — | — | — | — | 10.24 |
| H ₅ | . 5 | 2.15 | 2.22 | 2.22 | 2.24 | — | — | — | — | 2.23 |
| Ag | . 108 | 46.35 | — | — | — | 46.25 | 46.11 | 46.18 | — | 46.18 |
| S ₃ | . 48 | 20.60 | — | — | — | — | — | — | 20.49 | 20.49 |
| O ₆ | . 48 | 20.60 | — | — | — | — | — | — | — | 20.86 |
| <hr/> | | | | | | | | | | |
| | 233 | 100.00 | | | | | | | | 100.00 |

Ethylotrithionate of Copper. — $\text{CuO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$ — This salt can be prepared either by the double decomposition of the baryta-salt, or by dissolving carbonate of copper in the free acid. It crystallizes, both from its aqueous and alcoholic solution, in the form of greenish blue needles which are deliquescent. When dried at 100° C, it gave on analysis the following results :—

I. 6.55 grs. burnt with oxide of copper, gave 3.64 grs. of carbonic acid and 1.96 grs. of water.

II. 5.85 grs. similarly treated, gave 3.26 grs. of carbonic acid and 1.725 grs. of water.

III. 4.27 grs. cautiously ignited and exposed to a stream of air, gave 1.08 grs. of oxide of copper.

IV. 3.21 grs. ignited with a mixture of chlorate of potash and carbonate of magnesia, the product dissolved in hydrochloric acid and precipitated with chloride of barium, yielded 7.065 grs. of sulphate of baryta.

These numbers agree with the formula above given, as will be seen from the following calculation :—

| Calculated. | | | Analyses. | | | | Mean. |
|----------------|--------|--------|-----------|-------|-------|-------|--------|
| | | | 1 | 2 | 3 | 4 | |
| C ₄ | . 24 | 15.33 | 15.15 | 15.20 | — | — | 15.18 |
| H ₅ | . 5 | 3.19 | 3.32 | 3.27 | — | — | 3.29 |
| Cu | . 31.6 | 20.18 | — | — | 20.18 | — | 20.18 |
| S ₃ | . 48 | 30.65 | — | — | — | 30.20 | 30.20 |
| O ₆ | . 48 | 30.65 | — | — | — | — | 31.15 |
| <hr/> | | | | | | | |
| | 156.6 | 100.00 | | | | | 100.00 |

Ethylotrithionic Ether.— $\text{C}_4\text{H}_5\text{O}_3\text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$ —This ether was obtained by distilling a mixture of crystallized ethylotrithionate of baryta with sulphovinate of potash. On applying the heat of an oil bath, the crude ether came over, which, after being washed, dried by standing over chloride of calcium, and redistilled, presented the appearance of an oily yellow liquid slightly heavier than water, and possessing a disagreeable smell. It is insoluble in water, but miscible with alcohol in all proportions. Unfortunately I did not obtain a sufficient quantity of the ether to admit of the determination of its specific gravity and boiling point.

Ethylotrithionic ether, after being thoroughly dried by chloride of calcium, yielded the following analytical results:—

I. 3.72 grs. burnt with oxide of copper, gave 4.22 grs. of carbonic acid and 2.21 grs. of water.

II. 2.43 grs. burnt with magnesia and chlorate of potash, the product dissolved in hydrochloric acid and precipitated with chloride of barium, gave 5.50 grs. of sulphate of baryta.

The following calculation agrees with the above formula:—

| Calculated. | | | Analyses. | |
|-----------------|-----|--------|-----------|-------|
| | | | 1 | 2 |
| C_8 | 48 | 31.17 | 30.93 | — |
| H_{10} | 10 | 6.49 | 6.60 | — |
| S_3 | 48 | 31.17 | — | 31.05 |
| O_6 | 48 | 31.17 | — | — |
| | 154 | 100.00 | | |

Ethylotrithionate of Soda.— $\text{NaO},\text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\} + \text{HO}$.—This salt was also prepared by dissolving carbonate of soda in the free acid, evaporating to dryness, and treating with alcohol, which dissolves the ethylotrithionate of soda, whilst the excess of carbonate remains insoluble. The alcoholic solution, on evaporation in vacuo over sulphuric acid, yielded colourless crystals in the form of needles, which were, however, very small and not well defined. Determinations of the sulphur and sodium contained in this salt, after being thoroughly dried in vacuo, gave the following results:—

I. 8.40 grs. evaporated to dryness with sulphuric acid and ignited, gave 3.94 grs. of sulphate of soda.

II. 4.52 grs. burnt with a mixture of chlorate of potash and magnesia, the product dissolved in hydrochloric acid and precipi-

tated with chloride of barium, gave 9.90 grs. of sulphate of baryta.

These numbers agree sufficiently with the above formula.

| Calculated. | | | Analyses. | |
|----------------|----|-------|-----------|-------|
| | | | 1 | 2 |
| Na | 23 | 14.65 | 15.21 | — |
| S ₃ | 48 | 30.57 | — | 30.05 |

Sulphurous acid is also rapidly absorbed by zinc-methyl, a white crystalline body being produced as in the case of zinc-ethyl. I reserve, however, for a future communication, the complete history of this body, which contains most probably the zinc-salt of the first acid of this series—viz., the *Methylotrithionic Acid*. It is also highly probable that a complete series of organo-thionic acids will be produced by acting upon sulphurous acid with the various zinc-compounds of the alcohol-radicals.

The following is a list of the names and formulæ of the bodies which have been described in this memoir:—

Ethylotrithionic Acid. — $\text{HO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$

Ethylotrithionate of Zinc. — $\text{ZnO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\} + \text{HO}.$

Basic ethylotrithionate of Zinc. — $2(\text{ZnO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\} + \text{HO}) + \text{ZnO}, \text{HO}.$

Ethylotrithionate of Baryta. — $\text{BaO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\} + \text{HO}.$

Ethylotrithionate of Baryta dried at 100° C. — $\text{BaO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$

Ethylotrithionate of Silver. — $\text{AgO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{CH}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$

Ethylotrithionate of Copper. — $\text{CuO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$

Ethylotrithionate of oxide of Ethyl. — $\text{C}_4\text{H}_5\text{O}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\}$

Ethylotrithionate of Soda. — $\text{NaO}, \text{S}_3 \left\{ \begin{smallmatrix} \text{C}_4\text{H}_5 \\ \text{O}_5 \end{smallmatrix} \right\} + \text{HO}.$

III.—*On a new Volumetric Method for the Determination of Copper.*

By E. O. BROWN,

ASSISTANT IN THE CHEMICAL ESTABLISHMENT OF THE WAR DEPARTMENT.

A SERIES of experiments conducted by Mr. Abel in connection with the manufacture of bronze guns, involved the analysis of a large number of samples of gun metal, with which I was entrusted by him; and the much greater rapidity with which copper can be estimated by volumetric methods than by precipitation as oxide, led in the first instance to the selection of the method of Pelouze for adoption in these experiments, as the one of that class most likely to furnish trustworthy results.

The process in question, as originally described by Pelouze, is as follows:—

1 gramme of copper is dissolved in 5 or 6 grammes of commercial nitric acid, with the addition of a little water, if necessary; this solution is then mixed with 40 or 50 cubic centimetres of concentrated ammonia, raised to the boiling point, and a standard solution of sulphide of sodium added, until the blue colour disappears. During the whole of the operation, the liquid is kept in a state of gentle ebullition, fresh quantities of ammonia being added from time to time, to make up for the loss by evaporation. The use of the large quantity of ammonia keeps the boiling point of the liquid below the temperature of 80° C., beyond which it is not to be allowed to rise. The precipitate produced is expressed by the formula $\text{CuO}, 5\text{CuS}$; but it is stated to have a different composition, if the liquid, at the time of precipitation, is at a higher temperature than that above stated.

Following these directions as closely as possible, an attempt was made to standardize a solution of sulphide of sodium by means of electrolytically prepared copper. The results are given in the following table:—

| Quantity of Copper taken. | Measures of Sulphide of Sodium taken. | Calculated for 10 grains of Copper. |
|------------------------------|--|--|
| 9.10 | 82.5 | 90.6 |
| 9.10 | 82.8 | 90.9 |
| 9.10 | 82.2 | 90.3 |
| 9.10 | 82.5 | 90.6 |
| 14.48 | 136.0 | 93.9 |
| 13.29 | 121.5 | 91.4 |
| 13.21 | 121.8 | 92.2 |

It will be observed that there is little discrepancy between some of these numbers, and it is necessary therefore to notice, that when this is the case, the same quantities of copper were employed, and especial care was taken that the operation should be conducted in a precisely similar manner. In those instances in which there was any material difference in the amount of copper taken, and the quantity of sulphide of sodium necessary to obtain corresponding results was consequently unknown, the numbers obtained exhibit but little similarity. It should also be remarked, that whenever the contents of the flask were not shaken, but only agitated by boiling, a smaller amount of sulphide of sodium was required.

Considerable difficulty was experienced in deciding on the exact point at which the blue colour disappeared; since it was found, on agitating the liquid a short time after decoloration, that the colour was restored, and this continued to be the case for a considerable period after its first disappearance. Finding that little dependence could be placed on the disappearance of the blue colour, and observing that on reaching this point, the sulphide of sodium still gave a copious black precipitate, the addition of the sulphide of sodium was continued, until the copper was completely precipitated, and the following results were obtained:—

| Quantity of Copper taken. | Measures of Sulphide of Sodium taken. | Calculated for 10 grains of Copper. |
|------------------------------|--|--|
| 9·10 | 88·3 | 97·0 |
| 9·10 | 89·4 | 98·2 |
| 9·10 | 88·6 | 97·3 |
| 9·10 | 88·4 | 97·1 |
| 12·42 | 123·0 | 99·0 |
| 13·06 | 127·0 | 97·2 |

The same remarks apply to these determinations as to the former series.

The wide difference which exists between these numbers and the quantity of sulphide of sodium required, after the disappearance of the blue colour, to precipitate the whole of the copper, naturally led to the inference, that some chemical change, not hitherto noticed, had taken place.

The following experiments were consequently made:—

1st. A small quantity of a solution of sulphate of copper was diluted with 2 oz. of water containing a considerable excess of

ammonia, and the solution, which was of a light blue colour, was then boiled; on adding a drop of sulphide of sodium, a precipitate was produced, which was almost immediately redissolved, the solution changing to a greenish-brown. A second drop of sulphide of sodium produced a similar effect. On allowing the solution to stand five minutes, it became perfectly clear, its original blue colour being restored.

2nd. To a solution of copper, in all respects similar to the last, 3 drops of sulphide of sodium were added with the same effect as before. On the addition of the fourth drop, the precipitate ceased to redissolve and subsided in a few seconds, leaving the solution still of a brown colour, but of a lighter shade. The three next drops of sulphide of sodium each produced the same effect, after which it was found that the whole of the copper had been entirely precipitated.

3rd. A solution of copper was taken, similar to the last, but of double the strength. Two drops of sulphide of sodium produced no permanent precipitate, the solution retaining its original blue colour. The third drop changed the blue colour to a brown. No permanent precipitate was, however, produced till after the seventh drop, but only a darkening of the brown colour. On the addition of the seventh drop, a precipitate appeared, which, after much agitation of the liquid, gradually subsided, leaving the solution nearly colourless. The eighth drop again darkened the colour of the liquid, this effect also disappearing on violent agitation. The ninth drop produced no effect, the whole of the copper having been precipitated.

4th. To a similar solution of copper, but of four times the original strength, four drops of sulphide of sodium were added without changing the blue colour of the solution, the precipitate redissolving as soon as formed. The fifth drop produced a greenish-brown tint; but on allowing the solution to stand about half a minute, the original blue colour was restored. After the lapse of two or three minutes, a sixth drop was added; the precipitate redissolved, leaving the solution still brown. On the addition of the seventh drop the greenish-brown tint again made its appearance, gradually becoming darker with each successive drop until the fourteenth, when a permanent precipitate was first produced.

5th. To a solution of copper prepared as before, but eight times the original strength, eight drops of sulphide of sodium were

added before the blue colour changed to a brown, and a permanent precipitate was first obtained after adding fourteen drops.

In order to ascertain whether the amount of ammonia present influenced the solubility of the oxysulphide of copper, these experiments were repeated with a much larger, as well as with a smaller quantity of ammonia than usual, but with the same results.

From these results it is evident that the first quantities of oxysulphide of copper formed, are redissolved in the ammoniacal sulphate of copper, and that the amount so dissolved depends on the quantity of copper in solution.

The following experiment was then made in order to ascertain whether the oxysulphide of copper dissolved without undergoing any change :—

To an ammoniacal solution of copper, sulphide of sodium was added so long as the precipitate produced was redissolved; the solution was then boiled, and a drop of chloride of mercury added, which produced a white precipitate, showing that no sulphide existed in the solution.

It is evident, therefore, that oxidation of the sulphur must have taken place, which was proved to be the case by the following experiment :—

Sulphide of sodium was added to an ammoniacal solution of copper, until the blue colour was destroyed; the liquid was then agitated by boiling and the clear liquid decanted off: it was then acidified with sulphuric acid; and on boiling, a brown precipitate of sulphide of copper made its appearance, rendering it highly probable that the sulphur had passed into the state of hypsulphurous acid, or some of the lower oxides of sulphur.

It would appear that the oxysulphide of copper was oxidised at the expense of the protoxide of copper in solution, the suboxide being produced; whilst the repeated restoration of the blue colour on agitation of the liquid, as already described, clearly shows that suboxide of copper exists in solution. This is also further proved by the fact, that on filtering an ammoniacal solution of copper, to which sulphide of sodium has been added till the blue colour is destroyed, the blue tint immediately reappears in the filtrate, from oxidation of the suboxide having taken place in its passage through the pores of the filter.

In order to show still more clearly that the changes above mentioned take place, the following experiment was made :—

Sulphide of sodium was added to an ammoniacal solution of copper until the blue colour disappeared. After allowing the precipitate to subside, the colourless liquid was decanted off and divided into two portions, one of which was acidulated with sulphuric acid and boiled, when the brown precipitate, before mentioned, made its appearance. The other portion was passed through a filter, when it was observed that the blue colour immediately reappeared, and on acidifying no precipitate was produced; showing that in the latter case, by passing through the pores of the filter (which may be considered equivalent to a lengthened agitation), the sulphur had passed from the lower into the higher oxides, and the suboxide of copper into the protoxide.

Throughout these experiments, the ammoniacal solution of copper was boiled, previous to adding the sulphide of sodium.

The standard solution of sulphide of sodium used was made by dissolving 2 oz. of caustic soda in 1 quart of water. This solution was then divided into two equal parts, one of which was saturated with sulphuretted hydrogen; after mixing this saturated portion with the remainder of the solution of caustic soda, the whole was placed in a vessel capable of holding one gallon, which was then filled with distilled water.

It appears, therefore, that in determining copper by this method, the following changes take place:—

1st. That a portion of the oxysulphide of copper is oxidised at the expense of the salt of copper in solution, the latter being reduced to the state of suboxide, and consequently that a considerable quantity of copper must exist in the solution after the disappearance of the blue colour. From the great affinity of an ammoniacal solution of suboxide of copper for oxygen, it necessarily follows that agitation of the liquid must give rise to a constant reproduction of protoxide of copper.

2nd. That the sulphur of the sulphide of sodium also passes into solution in the form of hyposulphurous acid or some other low oxide of sulphur, thereby lessening the effect which the sulphide of sodium would otherwise produce.

It should also be remarked, that in adding sulphide of sodium to a solution of suboxide of copper, a smaller quantity of sulphur is required for a given amount of copper than in precipitating the protoxide.

These changes, in addition to the different composition of the oxysulphide of copper produced, according to the temperature of

the liquid at the time of precipitation, as stated by Pelouze, sufficiently explain the difficulty experienced in obtaining accurate results by the use of this method.

The conclusion to be drawn from the above results appears to be, that the method of determining copper by means of sulphide of sodium cannot be considered as chemically correct, inasmuch as an equivalent of sulphur does not precipitate a constant amount of copper; although it is evident from the great number of determinations detailed by Pelouze, that by long practice and skilful manipulation, considerable accuracy may, be attained, as, by adhering closely to the same mode of operating in all cases, the errors in each must necessarily be nearly alike.

A trial was next made of the method proposed by Parkes, which is thus described in Mitchell's Manual of Assaying.

"Take a given quantity of pure copper (say 10 grains), place it in a flask, and dissolve it in nitric acid, add ammonia in excess, and then make it into a bulk of 2500 grs. by measure (about 1-third of a pint) by the addition of water, although this is not absolutely necessary. Dissolve 1 ounce (avoirdupois) of pure cyanide of potassium, free from ferrocyanide or sulphide of potassium, in 6 oz. by measure of water; filter if necessary, and place the solution in a well-stoppered bottle till required for use. I then ascertain the quantity of this solution of cyanide of potassium required to decolorize the solution of copper by taking a given quantity in any graduated vessel—as a burette—and pour it by degrees into the solution of copper, adding the last quantity drop by drop until it is decolorized. This is very easily perceived, as there is no precipitate to interfere, and the operation is conducted at the ordinary atmospheric temperature."

In the course of the experiments made by this method, it was observed that the bleaching effect of the cyanide of potassium was gradual in its operation; and it was found that on allowing an ammoniacal solution of copper, to which cyanide of potassium had been added (but not sufficient to destroy the blue colour) to stand for a short time, it became completely bleached; the quantity of cyanide of potassium necessary to produce complete decoloration being in proportion to the length of time taken in the operation.

Under these circumstances, the point at which the addition of the cyanide of potassium should cease became a matter of great uncertainty, and as this method did not promise more accurate

results than those obtained by sulphide of sodium, it was not pursued further.

In the course of a number of experiments made with the view of obtaining some other method of determining copper with greater certainty than either of the preceding, the reaction of iodide of potassium upon a salt of copper, which results in the production of subiodide of copper and free iodine, appeared likely to be available for this purpose.

Knowing with what accuracy iodine may be determined by means of sulphurous acid, according to the method proposed by Bunsen, it seemed reasonable to expect, that by determining the amount of iodine liberated by the action of iodide of potassium upon a salt of copper, an equal degree of accuracy could be attained in the estimation of copper.

Bunsen's method for the determination of iodine, is to add an excess of a very dilute solution of sulphurous acid of known strength, and to estimate the amount of sulphurous acid unacted upon, by a standard solution of iodine. On calculating the amount of SO_2 in this state of dilution, required for the determination of 10 grs. of copper, I found the quantity would be inconveniently large, and that the use of a stronger solution was not practicable. Whilst endeavouring to obviate this difficulty, it occurred to me that the reaction of hyposulphurous acid on iodine, which results in the formation of hydriodic and tetrathionic acids, might be substituted for that of sulphurous acid; and a number of experiments were instituted to ascertain whether this was the case, the results of which proved that iodine may be determined by means of hyposulphurous acid with as great a degree of accuracy as by Bunsen's method, and moreover, with the advantage of requiring only one standard solution instead of two, and that of a more stable character than a solution of sulphurous acid.

The method finally adopted for determining copper is as follows :—

Ten grains of copper are dissolved in dilute nitric acid, and the solution boiled until free from nitrous acid; it is then diluted with about an ounce of water, and carbonate of soda added until a portion of the copper is precipitated. Pure acetic acid is then added in excess, and the solution poured into a flask capable of holding about 12 oz. About 60 grains of iodide of potassium are then thrown into the flask, and sufficient time having been allowed for the crystals to dissolve, a standard solution of hypo-

sulphite of soda is added until the greater part of the iodine has disappeared, which is indicated by the liquid changing from a brown to a yellow colour. A little clear solution of starch is then added, and the addition of the hyposulphite of soda cautiously continued until no further effect is produced.

The bleaching effected by the last portions of hyposulphite of soda may be best seen by allowing the drops to fall into the centre of the flask whilst the liquid is in motion, when streaks of a lighter colour will be produced so long as any iodine remains.

When the quantity of iodide of potassium employed was less than six times the weight of the copper to be determined, satisfactory results were not obtained.

Care must be taken that the iodide of potassium employed is free from iodate of potash, and that the acetic acid contains no sulphurous acid.

The solution of starch should be made by boiling with a large quantity of water, any undissolved portions allowed to subside, and the clear liquid only used.

A solution of hyposulphite of soda obtained by dissolving about 4000 grains of the salt in two gallons of water, was standardized by means of electrolytically prepared copper. The burette employed was capable of holding 1500 grains of solution, each drop corresponding to about 0.006 of a grain of copper.

The numbers obtained were as follows:—

| Grs. of Copper taken. | Measures of Standard used. | Calculated to 10 grs. of Copper. |
|--------------------------|-------------------------------|-------------------------------------|
| 8.02 | 124.6 | 155.3 |
| 7.44 | 115.7 | 155.4 |
| 7.67 | 119.2 | 155.4 |
| 8.32 | 129.4 | 155.5 |

Another quantity of standard solution gave the following:—

| | | |
|------|-------|-------|
| 8.38 | 131.4 | 156.8 |
| 8.78 | 137.5 | 156.7 |

Several experiments were made in order to ascertain to what extent the results obtained by this process were liable to error from irregular manipulation or changes of temperature, the same amount of copper (9.10 grains) being used in each experiment.

In the first, the directions above given were strictly observed; the quantity of standard solution required was 134.4 measures.

In the second, time was not allowed for the crystals of iodide of potassium to dissolve before beginning to add the hyposulphite of soda ; the number of measures required was 134·3.

In the third, the solution of copper was diluted with as much water as could be conveniently contained in the flask ; the number of measures required was 134·5.

In the fourth, the solution of copper was as concentrated as possible ; the number of measures required was 134·4.

In the fifth, after adding the crystals of iodide of potassium, the solution was shaken up and allowed to stand for a quarter of an hour before proceeding with the hyposulphite of soda ; the number of measures required was 134·3.

In the sixth, the operation was conducted at 150° F. ; the number of measures required was 131·2. The flask in this experiment was observed to be filled with the vapour of iodine.

In the seventh, the operation was conducted at the temperature of 90° F. ; the number of measures required was 134·0.

From these experiments it is evident that slight differences in the mode of manipulating do not in any way affect the results so long as the solution is not heated.

The presence of tin, lead, iron, or zinc in small quantities, is also immaterial.

When the alloy in which the copper is to be determined contains a large proportion of lead or iron, these metals should be separated previous to the determination of the copper, since the yellow precipitate of iodide of lead and the red colour of the acetate of iron render it difficult to distinguish the effect produced by the last quantities of hyposulphite of soda.

The following determinations of copper in a number of specimens of gun-metal, taken from castings at the Royal Gun Factory at Woolwich, will serve to show the accuracy which may be obtained by this method :—

| Grs. of Metal taken. | Measures of Standard used. | Per centage of Copper in alloy. |
|-------------------------|-------------------------------|------------------------------------|
| 10·13 | 139·7 | 90·79 |
| 9·99 | 137·7 | 90·66 |
| 10·54 | 145·0 | 90·59 |
| 10·46 | 144·1 | 90·68 |
| 10·09 | 139·3 | 90·90 |
| 10·52 | 145·5 | 91·09 |

| Grs. of Metal taken. | Measures of Standard used. | Per centage of Copper in alloy. |
|-------------------------|-------------------------------|------------------------------------|
| 10·23 | 141·9 | 91·32 |
| 10·15 | 140·6 | 91·23 |
| 10·52 | 146·7 | 91·79 |
| 10·40 | 144·9 | 91·75 |
| 9·93 | 136·4 | 90·48 |
| 10·14 | 139·3 | 90·42 |
| 10·19 | 141·1 | 91·21 |
| 10·26 | 142·3 | 91·36 |
| 9·79 | 136·6 | 89·17 |
| 9·82 | 137·0 | 89·19 |
| 9·96 | 142·7 | 90·78 |
| 10·05 | 144·2 | 90·72 |
| 10·00 | 144·6 | 91·60 |
| 10·10 | 146·2 | 91·52 |

It may, therefore, be safely stated that copper can be estimated with ease and certainty by this method to within $\frac{1}{10}$ or $\frac{2}{10}$ per cent., and that the method possesses the advantage over those hitherto used of being likely to give similar results in the hands of different manipulators.

IV.—*On the Action of Light upon Chloride of Silver.*

BY FREDERICK GUTHRIE, B.A., Ph.D.

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THE blackening produced by light upon chloride of silver in the moist state was ascribed by Scheele to the liberation of chlorine, and the deposition of metallic silver. He proved that the blackened mass was only partially soluble in ammonia, and that the portion which remained undissolved by this re-agent was soluble in nitric acid. Daniell and others considered the blackening to be due to the formation of oxide of silver, imagining the decomposition of the water present by the chlorine, to be accompanied by a corresponding oxidation of the reduced silver. Others, again, have supposed the formation of a subchloride.

The few experiments which I subjoin tend, unmistakeably, to support the view originally advanced by Scheele.

(1.) Two or three grammes of dry chloride of silver were sealed in a glass tube, and exposed to direct and diffused sunlight. There was increased tension in the tube. Chlorine was shown, by the iodine test, to be present in the free state.

(2.) A portion of chloride of silver, dried at 100° , was introduced into a perfectly dry tube. The tube being then half-filled with pure and dry benzole, and heated until the boiling of the benzole had expelled all the air, was hermetically sealed, and exposed with agitation to the light. The rapid blackening which the chloride here underwent, proved the presence of oxygen to be unnecessary.

(3.) Four or five grammes of moist chloride of silver were sealed in a tube. The tube was half filled with water, and hermetically sealed. After exposure to the light for ten or twelve days, with frequent agitation, it was opened, the contents thrown upon a filter, and washed with cold water. On adding nitrate of silver to the filtrate, a precipitate of chloride of silver was formed. The grey mass on the filter was treated with strong ammonia until the latter ceased to dissolve any more of the unaltered chloride. There remained on the filter a slaty grey body, which, in the dry state, took the metallic lustre under the pestle. This body was soluble in nitric acid, not reprecipitable by ammonia, but precipitated by dilute hydrochloric acid. The non-precipitation of the nitric acid solution by the most gradual addition of ammonia, seemed already to point to the absence of chlorine.

(4.) About ten grammes of the moist chloride were introduced into a tube of $1\frac{1}{2}$ ft. in length, and $\frac{3}{4}$ in. internal diameter. After adding water and sealing, the tube was exposed as before. The supernatant liquid was poured off, and the mass washed by decantation. The hydrochloric acid was thrown down by nitrate of silver. The chloride of silver was estimated on a weighed filter

(dried at 100°C.) $\text{Ag Cl} = 0.2125 \text{ gm.}$

The washed material from the tube was digested with strong ammonia. The slaty-grey residue which subsided, leaving the liquid above quite clear, was collected upon a weighed filter and washed, first with ammonia, then with water

(dried at 100°C.) Grey substance = 0.1756 gm.

This substance assumed the metallic lustre under the burnisher. It dissolved in warm nitric acid, decomposing the latter. The substance, together with the filter, was thrown into strong nitric acid: after digestion and due dilution, it was filtered. The silver was thrown down by dilute hydrochloric acid, collected on a weighed filter and estimated.

(dried at 100°C.) $\text{Ag Cl} = 0.2254 \text{ gm.}$

Supposing, now, the grey substance obtained to have been metallic silver, it should have given 0.2333 gm. of chloride. The amount actually obtained, though too small, is yet sufficiently near to the calculated quantity to show that the original chloride of silver subjected to the light, had really undergone decomposition into chlorine and metallic silver. That the chloride of silver obtained from the hydrochloric acid, found in the tube on breaking it open, was somewhat smaller than that from the silver, was probably due to an escape of a portion of the free acid by evaporation during manipulation.

(5.) About twelve grammes of the chloride of silver were introduced into a tube; the tube was then half filled with fuming nitric acid, sealed, and exposed as before. On opening the tube it was found to contain hydrochloric acid. The chloride was found to have undergone a blackening quite as deep as that which had taken place in chloride of silver surrounded by water, which was exposed to the same light for the same time. On treating the contents as in experiment (4), there was found

| | | | | | |
|----------------|---|---|----------------|---|--------|
| Grey substance | . | . | . | = | 0.1643 |
| which gave | . | | Ag Cl | = | 0.2040 |

The quantity, supposing the substance to have been silver, should have been

$\text{Ag Cl} = 0.2183$

This is sufficiently near to show that the substance in question was nothing else than metallic silver.

(6.) Confirmatory of experiment 5.

(7.) The circumstances were as in experiment 5, excepting that the nitric acid employed was more dilute.

On treating the contents as in experiment 4, I found

Grey substance = 0.2207 gm.

and this gave

$\text{Ag Cl} = 0.2870$

instead of the calculated quantity

$$\text{Ag Cl} = 0.2932$$

In experiments 4, 5, 6, the grey substance when dry assumed the metallic lustre under the burnisher.

The fact that the chloride of silver was reduced to the metallic state, even in the presence of nitric acid, was quite unexpected. I found that neither by removing the affected mass from the light, and agitating it, nor even by warming it, was the original whiteness restored. Indeed the silver was only very gradually attacked by boiling nitric acid, unless the undecomposed chloride had been previously removed by the action of ammonia. It seems as if the light, in reducing the silver *in spite* of the nitric acid, had thereby thrown it into a more passive state, and that only after contact with the alkaline ammonia, was its original basic condition restored.

The chloride of silver used in these experiments was in every instance washed by decantation, in order to avoid the presence of organic matter.

V.—*On some Thermo-electrical Properties of the Metals Bismuth and Antimony when used as single elements.*

BY RICHARD ADIE, LIVERPOOL.

I WISH to shew that when bars of bismuth are cast so as to break with a smooth cleavage surface, or with a granular surface, they possess different thermo-electrical properties. Also that bars of antimony, under similar treatment, partake in a lesser degree of the same character.

Square bars of bismuth 7 inches long by .15 of an inch square, were cast in a brass mould which opened along two of the opposite diagonal edges of the bar to admit the removal of the casting.

Bismuth cast in this mould, previously heated to the melting temperature of the metal and slowly cooled, broke with a fracture which presented a large shining surface; and when cast in the mould cold, the fracture of the bars presented a surface similar to some of the common varieties of cast iron. It was with these two classes of bars that I obtained the different results noted in the experiments.

Antimony bars were prepared in like manner, but the fracture of those cast at the highest temperatures was never free from the effect produced by the chilling of the sides of the mould.

The results are arranged in the following table. The signs + — are put opposite the bars when they were negative or positive, according to the direction in which the heat was made to cross the joint.

| First Bar. | Sign. | Second Bar. | Sign. | Description. |
|--|--------|--|--------|--|
| Bismuth, cast of large grain | + — | Bismuth, cast of large grain | + — | This was a bar broken in two, the surfaces for contact being slightly rounded with a file. Heat and electricity crossed the joint in the same direction. |
| Bismuth, cast of small grain | + — | Bismuth, cast of small grain | + — | This was a broken bar; the broken surfaces for contact being rounded. Heat and electricity crossed the joint in opposite directions. |
| Bismuth, cast of large grain | + — | Bismuth, cast of small grain | + — | Heat and electricity crossed the joint in the same direction. |
| Antimony, large grain | + — | Antimony, large grain | + — | This was a broken bar; the broken surfaces rounded. Heat and electricity crossed the joint in the same direction. |
| Antimony, fine steel-like fracture | — | Antimony, fine steel-like fracture | + — | These were two separate castings. The direction of the flow of heat across the joint did not govern that of the electrical current generated. |
| Antimony, large grain | + — | Antimony, fine steel-like fracture | + — | Separate castings. Heat and electricity crossed the joint in the same direction. |

When a thin leaf of bismuth was nipped between the two antimony surfaces, heat and electricity immediately crossed the joint in opposite directions.

I Chloride Salt



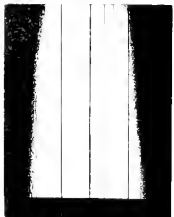
H G F b e D B

VII Manganous Chloride



F b e D B

XIII Copper Salt



H G F b e D B

XIX Chromate of Potash



F b e D B

II Nitrate Salt



G F b e D B

VIII Ferrous Oxide of Potash



b e D B

XIV Ferric Sulphoguanate



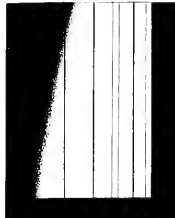
G F b e D B

XX Bichromate of Potash



b e D B

III Ferrous Salt



G F b e D B

IX Chromate of Copper



F b e D B

XV Dilute Ferric Sulphate



G F b e D B

XXI Neutral Lithmus



G F b e D

IV Potassium Salt



H G F b e D B

X Al' Cobalt salt



H G F b e D

XVI Ferric Manganate



H G F b e D B

XXII Alkaline Lithmus



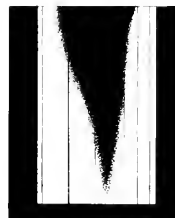
G F b e D B

V Chloride of Copper



F b e D

XI Aquous Cobalt Salt



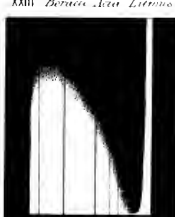
H G F b e D B

XVII Ferric Oxide



G F b e D B

XXIII Ferric Acid Lithmus



H G F b e D

VI Ferric Oxide



F b e D B

XII Permanganate of Potash



G F b e D B

XVIII Ferric Oxide



G F b e D B

XXIV Acetic Lithmus



G F b e D B

A. Chromium Salt



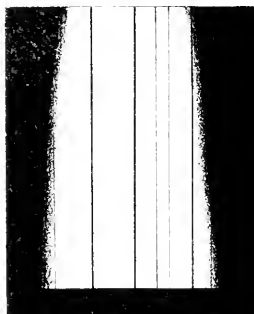
H G d F b E D B

VII. Molybdic Chloride



F b E D B

XIII. Copper Salt



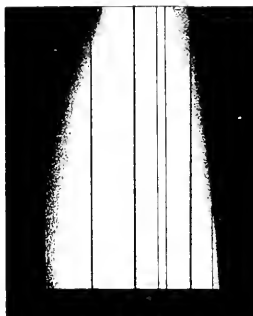
H G F b E D B

XIX. Chromate of Potash



F b E D B

II. Nickel Salt



G F b E D B

VIII. Ferricyanide of Potass



b E D B

XIV. Ferrie Sulphocyanide



G F b E D B

XX. Dichromate of Potash



b E D B

VI.—*On the use of the Prism in qualitative analysis.*

BY DR. J. H. GLADSTONE, F.R.S.

THE ordinary methods of qualitative analysis depend on a system of exclusion. We first determine that the substance analysed does not contain any member of certain large groups, but consists of one or more members of certain other groups: and these we sub-divide, excluding one division after another, till we arrive at the individual member or members, and these are at length distinctly recognized by special characteristics, or perhaps, special tests. In this process, the indications of colour have hitherto played but a very subordinate part. They have, indeed, been esteemed most valuable when we come to special characteristics or tests, but in any previous stage of the process they are not relied on. Thus, to take an instance:—if, in mineral analysis, we meet with a metal not precipitable by hydrochloric or hydrosulphuric acids, but thrown down by sulphide of ammonium, as well as by ammonia or potash, as a gelatinous oxide soluble in the fixed alkalis, the green colour of the oxide at once confirms the conclusion that the metal is chromium; but if we see an unknown salt or mixture of salts of a similar green colour, we do not conclude that it contains chromium, nor, if we fail to recognize that colour, do we necessarily infer that chromium is absent. We know indeed on the one hand that there are many other green salts, and on the other hand we speak of some of the salts of chromium as not green, but red, or blue.

Now this arises in a great measure from merely observing the colour as it appears to the untutored and unaided eye. It should be remembered that the colour of an object is the resultant of the various rays of the spectrum which it reflects or transmits, or, perhaps more philosophically, of the various rays which it does not absorb. Yet that colour may be produced by the union of totally different rays; thus—one substance may appear indigo, because it reflects the indigo ray, another, because it reflects the blue with a little red.

This can evidently be determined only by the prism; and in examining the coloured solutions of various salts by that instrument, I have been led to the conviction that chromatic phenomena may be relied on in analysis to an extent, which I think has been

rarely, if ever, suspected. There is this advantage too in such a mode of determining the character of a body, that not a particle of it need be used up in the analysis, nor altered or destroyed by the addition of reagents—a matter of no slight importance when we have to deal with organic compounds, or valuable mineral substances. Mr. Pearsall, and perhaps others, have used the prism with success in particular cases; Professor Stokes has claimed for it a place in the laboratory;* and it is to draw the attention of chemists still more decidedly to this mode of analysis, and to lay down some generalized observations, that I have written the present paper.

The use of the prism is not difficult. Many different methods may be pursued. Professor Stokes examines the chromatic effect of some metallic oxides by fusing them with a bead of micro-cosmic salt, and “viewing through a prism the inverted image of the flame of a candle formed by the bead, the latter being so held as to be seen projected on a dark object.”† In examining a powder or small crystal I have found the following plan answer:—A plate of glass is held in the sun-light in such a position that few, if any, rays are reflected by its surface to the eye, while through it is seen a piece of black cloth or paper in the shade. On the glass is then placed a thin line of the powder, or a small crystal or two, which will of course appear brightly illuminated against a dark ground. By viewing this through a prism, the line of powder will be expanded into a ribbon, or the crystal into a broad image, which, by its varied colours, will show what rays are reflected. Another way of examining a solid substance is by looking at it with a prism through a slit in a black card. But these are inelegant and inexact methods of observation as compared with what is practicable when liquids are examined. We have then to deal especially with transmitted light. The common method is to view by a prism a slit in the window shutter, seen through a glass vessel containing the liquid; but this method generally fails to give intelligible results unless attention be paid to the strength of the solution, and the thickness of the stratum

* Since the above was written, my attention has been called to the fact that Mr. Talbot (*Ed. Journ. Sci.* v, 77, and *Phil Mag.* iv, 114, and ix, 3), and Mr. Crookes, have recommended the prism as a means of distinguishing the different flames given by metallic salts; but this plan of procedure, though doubtless very accurate in certain cases, is of limited and difficult application.

† *Phil. Trans.* 1852, p. 522.

through which the ray passes ; for in most cases the different rays of light are not absorbed immediately on their entering a liquid, but when they have penetrated it to a greater or less distance, and they disappear, not suddenly, but by becoming gradually fainter and fainter. Hence, for holding the solution, I am in the habit of employing, not a vessel with parallel sides, but a hollow wedge of glass held in such a position that the slit in the window-shutter is seen traversing various thicknesses of the liquid from the thinnest possible film to a stratum of perhaps three-quarters of an inch in thickness. This line of coloured light does not then appear uniform : as will be at once foreseen, it varies in intensity from almost pure white to a deep shade ; and it frequently displays variations of a much more unexpected character, being of a totally different colour in one part to what it is in the other ; for instance, blue at one end of the line, and red at the other, every shade of purple intervening. When this coloured line of light is analysed by a prism, very remarkable appearances often present themselves : the whitish portion of the line, where the light traverses very little liquid, will be expanded into a ribbon, differing but little from the spectrum given by unaltered light ; but as the line is viewed through deeper and deeper portions of liquid, some rays are seen to diminish in intensity, others gradually to die out, while others, again, almost immediately disappear, giving place to perfect darkness. If the prism be a tolerably good one, the slit narrow, and the day not too dull, the most visible of "Fraunhofer's lines" will be readily seen running like black threads along this coloured ribbon, and serving to mark with perfect accuracy what rays are transmitted, and what absorbed. The appearances thus presented to the eye can be easily transferred to paper, thus giving at one glance the optical character of the rays which penetrate every different thickness of the solution.

From the numerous observations I have made in this manner, it may be laid down as a general rule that *all the compounds of a particular base, or acid, have the same effect on the rays of light*. Occasionally, but very rarely, a glaring exception occurs ; and much more frequently there are certain variations in degree—the same rays being absorbed, but to a slightly different extent, as compared with one another.

This truth has been partially recognized for a long time : thus every chemist knows that the salts of nickel are green, and those of zinc colourless ; but there are other cases in which it is not so

evident—in fact, where apparent exceptions occur. Some of these anomalies are here discussed.

Chromium Salts.—It has been already stated that some salts of chromium, are called, not green, as the generality are, but red or blue. This remark applies to both solid and dissolved salts. Yet when these various-coloured solutions are examined in the way described above, they all give the same, or very nearly the same, spectrum, and that a very characteristic one. See Fig. 1. The thinnest stratum of liquid suffices to cut off all the yellow rays, and nearly all the indigo and violet: as the thickness increases, the transmitted light appears more and more concentrated about two points, the one at the least refrangible end of the spectrum, the other between the lines *F* and *b*. It is there of a bluish green tint, and is at first supported on either side (if such an expression may be allowed) by blue and by yellowish green, which, however, soon disappear, leaving it also gradually to be absorbed, while the red, which was at first accompanied by orange, passes through the deep liquid alone, and with almost undiminished brilliancy.

The result of this great penetrating power of the red ray as compared with the green and blue, is, that the chloride, nitrate, sulphate, sulphocyanide, and other salts of chromium, which appear green in tolerably dilute solution, appear red when we look through a strong or a very deep solution. This circumstance has been noticed by Schr  tter and others, and has been explained by Sir John Herschel,* who gives the name of dichromatism to the phenomenon. Now the acetate, though it absorbs the same rays as the above-mentioned salts, does not transmit the green so readily; hence it appears usually red, and it is only in very thin or weak solution that it assumes the green appearance: while the “red potassio-oxalate” absorbs the green so speedily that that colour never preponderates, and the thinnest stratum never approaches it nearer than a bluish red. Yet these present a prismatic appearance scarcely distinguishable from that of the salts previously described.

Again, there are two apparently isomeric modifications of some chromium salts, which differ in colour as well as in chemical properties. Thus it is the blue, and not the green sulphate,† that combines with sulphate of potash to form potash

* Ed. Phil. Trans. Vol. ix.

† Berzelius and Schr  tter have both proved this.

chrome alum : but this double salt, though it appears so unlike one of the green compounds to the unaided eye, gives the same peculiar prismatic appearance. The "blue potassio-oxalate," also, though the thinnest stratum of its solution is a faint bluish purple, exhibits the same two maxima of transmission, the only perceptible difference being that the blue space near *F* is very brightly illuminated. An easy method of observing these two modifications is to take an ordinary green solution of nitrate of chromium, divide it into two parts, and boil one of them for a few minutes with an excess of nitric acid. When cool again, the contrast between the two by daylight will be very great, the one a deep green, the other a bluish purple ; but if examined in the way described above, they will present very nearly the same prismatic appearance, the only difference being that the acid solution transmits more light, at least, more of the red and blue rays.

Thus the various chromium salts, though optically very different to the unaided eye, present almost exactly the same appearance, and that a very characteristic one, when examined in the manner suggested.

Cobalt Salts.—We are accustomed to speak of blue and red salts of cobalt ; but this difference depends really on the state of hydration, and the prism reveals an analogy, otherwise unsuspected, between the two colours.

The chloride, and other salts, when anhydrous, are blue. Alcoholic solutions of the chloride, and acetate are also blue.

The chloride, and other salts, when hydrated, whether in the crystallized condition, or actually dissolved in water, are red. The only exception to this, with which I am acquainted, is the sulphocyanide, which crystallizes of a magnificent blue, and gives a saturated aqueous solution, also of a blue colour. The addition of more water, however, gradually changes this to the same red as any other solution of a cobalt salt ; while the subsequent addition of alcohol restores the blue colour to a greater or less degree.

A blue salt of cobalt, such as smalt blue glass, or an alcoholic solution of the chloride, is dichromatic, and if the light reaching the eye has traversed a sufficiently large quantity, it appears red. The alcoholic solution examined in the manner described above, exhibits a very remarkable appearance. It is represented in Fig. 10. The extreme red ray penetrates with the greatest facility, indeed it is much more visible where the stratum is thick, than where it is thin, because in the latter case the neighbouring orange,

by its great luminosity renders it almost imperceptible. Immediately succeeding this narrow red ray, is a thin space of perfect absorption, followed by another red ray, which penetrates a short distance, and by the orange which penetrates a little farther. Then, coincident with the line *D*, but considerably broader, is a space of absolute blackness, while the rays between it and *E* advance far into the liquid, yellow and bright green. The succeeding rays, till near *F*, are greatly reduced in brilliancy on their first entering the liquid, yet they succeed in penetrating it to a considerable distance as a faint bluish green. The blue rays are admitted very readily, the indigo still more so, and the violet advances further yet into the liquid, the lines *F*, *d*, and *G* being very discernible.

A red solution of a cobalt salt gives the appearance represented in Fig. 11. The red and orange rays are transmitted with the greatest ease, the line *D* is strongly marked, the yellow penetrates not quite so far, while the rays between *E* and *F* are very faint, though they are not soon wholly absorbed; the blue passes readily, and the indigo and violet show a constantly increasing power of penetration. The lines *d* and *G* are very distinct.

On comparing the prismatic appearances of these two classes of cobalt salts, it will be at once perceived that both the anhydrous and the hydrated salts transmit the extreme rays of each end of the spectrum most freely. They are analogous also in the faint greenish blue which penetrates for some distance though with but feeble luminosity, between *E* and *F*. Through a strong and deep solution of either the red ray alone passes. There are, however, some equally well marked points of contrast: the orange ray is almost immediately absorbed by the blue salt, but is transmitted with the greatest facility by the red; and the maximum of absorption is, in the one case, about *B*, and in the other about *F*.

Copper Salts.—Anhydrous copper salts present a variety of colours: hydrated crystals, or solutions, are generally blue, but sometimes green; yet the green salts themselves become blue when dissolved in a sufficient amount of water.

Alcoholic solutions not merely of the green chloride, but of the blue acetate, are green. When examined by the prism, they give the appearance delineated in Fig. 5. A thin stratum, even of a very dilute solution, cuts off at once the least refrangible red rays, and the whole of the more refrangible half of the spectrum. The rays from a little before *D* to a little before *F* are transmitted,

and penetrate indeed with almost undiminished luminosity through a very great thickness of solution, appearing to the eye of an almost uniform bright green colour. At first they are accompanied on either side by a little red and blue, but these are soon absorbed. This description applies equally to a saturated aqueous solution of the chloride.

The blue salts of copper, and all aqueous solutions, if sufficiently diluted, give an appearance not differing widely from the normal spectrum. The rays about the blue portion are admitted very freely, while those at each end are partially but not wholly absorbed. They differ considerably in the extent to which these other rays are suppressed; the consequence of which is that solutions of some salts, for instance, the acetate, appear of a much deeper blue than solutions of other copper salts, though of corresponding strength. Fig. 13 is taken from the acetate.

Most, if not all, double salts of copper, (as, for instance, the double sulphate of copper and potash, or ammonia,) are nearly identical with the simple salt both in the character and intensity of the colour. The true ammoniacal salts of copper, which appear so intensely blue, must be distinguished from these, as they appear to contain the copper in some state of combination with the elements of ammonia, and they give a very different prismatic appearance. The maximum of absorption is about *D*, the red and the green rays are transmitted a short distance, while the indigo, violet, and still more refrangible invisible rays, are suffered to pass most freely.

Ferric Salts.—An examination of the various ferric salts is very instructive, in respect to the limits within which there may be diversity in the action of different compounds of the same base on the rays of light. It is well known that they are for the most part red, yet there is an immense difference in the degree of redness exhibited by different salts when dissolved. Thus the nitrate is almost colourless, unless in strong solution; the acetate is vastly redder; while the meconate and sulphocyanide are most intense in their colour. Yet the ferric chloride is orange-yellow, and a solution of the citrate sometimes appears green. In all these cases, however, there is an absorption more or less complete, of all the more refrangible rays, leaving the least refrangible to penetrate almost any thickness without much diminution. This great transmissibility of the red ray causes

those salts which appear of another colour in dilute solution to be dichromatic.

On closer inspection, several groups of ferric salts may be distinguished; all of which, however, agree in this permanence of the extreme red.

1. Those ferric salts which are red at any thickness, for instance, the sulphocyanide. An extremely thin film, of a strong aqueous or alcoholic solution of this compound, permits all the rays of the spectrum to pass; but suddenly all are cut off except those less refrangible than the line *D*, and after awhile the extreme red alone penetrates. See Fig. 14. If a weaker solution of ferric sulphocyanide be examined, there will be observed a tendency of the blue ray to manifest itself; for this salt, as is well known, is altered by the addition of water. See Fig. 15.

2. Solutions of the ferric chloride and citrate give the same prismatic spectrum, at least as far as configuration is concerned, though they appear very different to the unaided eye. The chloride is of an orange-yellow, and whether the solution be strong or weak, deep or shallow, it appears of very nearly the same tint and depth of shade. The citrate, on the contrary, if little be presented to the eye at once, is green; if more, it is warm brown; if still more, red. In each case the prism shows that all the rays, from the least refrangible to *E* are freely transmitted; at *b* the blue begins to fringe the green, but it is soon absorbed; while every ray beyond that is cut off absolutely, the violet by even a thin stratum of a very dilute solution. See Fig. 6. There is a difference, as will be anticipated, between the intensity of the rays transmitted by these two salts: the chloride admits the orange and yellow to almost any distance with apparently undiminished luminosity; while the citrate transmits the green rays, subduing the intensity of the others to such a degree that the yellow space at least appears green also.

3. The compounds of ferric oxide with meconic acid and its derivatives form a very distinct group. The *meconate* itself is dichromatic, appearing red *en masse*, but of a peach-blossom colour when in a very thin stratum. The prismatic appearance is given in Fig. 16. The red and orange rays are transmitted freely, the yellow and green are rather soon absorbed; about *F* no ray whatever enters the solution, but the more refrangible are admitted, gradually fade, and disappear all at about the same distance, and

rather abruptly. The *comenate* of iron gives a prismatic appearance which is almost identical, see Fig. 17; but the more refrangible half of the spectrum is not so luminous, I think; and the indigo ray penetrates farther than its neighbours. The maximum of absorption is about half way between *b* and *F*. The ferric *pyromeconate* appeared indistinguishable by the prism from the *comenate*. There are two compounds of comenamic acid and ferric oxide, the one affording an intense red, the other a still more intense purple solution. Yet different as these are to the unaided eye, they give the same configuration of spectrum when examined with a prism, and this configuration differs from that of the *comenate*, only in the same manner as the latter differs from that of the *meconate*. It is represented in Fig. 18. The *acid comenamate*, which is red, transmits the red, orange, green, and blue, as its congeners do, but allows the violet to penetrate farther even than the indigo. The *basic comenamate*, which is blue-purple in thin, and red-purple in thick stratum, transmits the same rays as the acid salt; but the luminosity of the more refrangible half of the prismatic appearance is much greater, and it penetrates farther.

The ferric gallate, ferrocyanide, and ferridcyanide are perfectly different to other salts of the same base in their action on the rays of light.

Chromates.—It is well known that chromic acid and its compounds are all highly coloured, but that the colour is not the same in all cases; yet the prism, while it indicates a perfect difference between the compounds of chromic oxide and those of chromic acid, exhibits a close analogy between the various chromates. Thus bichromate of potash is red, while the neutral chromate is yellow; but a glance at Figs. 19, 20, will show that their prismatic appearances bear a certain analogy. The red salt in thin stratum permits the least refrangible half of the spectrum to pass, but cuts off at once every ray more refrangible than *F*; as the stratum of liquid increases, it absorbs the slight amount of blue, and the red also, until nothing is visible except a bright band of orange and yellowish green, extending equal distances on each side of *D*, but not quite including either *B* or *E*. The yellow salt admits a somewhat wider spectrum: as seen through the hollow wedge, it presents an uniform band of light, extending the whole length, and consisting of the ordinary spectrum as com-

prized between *A* and *F*; only when it is very thin a little more blue and red appear.

Both chromic acid, and bichromate of silver, though red in the solid state, give orange-yellow solutions, and prismatic appearances almost identical with that presented by yellow chromate of potash.

Litmus.—As an instance from the organic world, litmus may be selected. Every tyro in chemistry is familiar with the fact that this substance is blue when neutral, more blue when alkaline, red when acid, and of a peculiar wine-red colour when affected by either carbonic or boracic acid. Now the prismatic appearances, presented by these differently coloured kinds of litmus, are only modifications of a common type.

If a neutral solution of litmus be placed in the hollow wedge, its dichromatic character becomes at once evident: the thin portion appears blue, the thick portion red, while every shade of purple intervenes. If a line of light passing through these various thicknesses be examined by a prism, it shows that the red penetrates any distance almost unchanged, that the orange is more readily absorbed, that the rays a little less refrangible than *D* are absolutely stopped, that the green is transmitted to a considerable distance, and is very luminous, that the blue is transmitted not quite so far, and the indigo and violet are still more quickly absorbed. See Fig. 21. If to this solution of litmus, an alkali, whether fixed or volatile, be added, the passage of the red, yellow, green, and violet rays is little, if at all, affected, but the liquid becomes more opaque to the orange ray, and far more transparent to the blue and indigo. See Fig. 22. The extent to which this alteration takes place depends on the amount of alkali present. If to the solution of neutral litmus, boracic acid be added, it manifests its presence by causing the indigo and violet to be more freely transmitted than even the blue, but besides this it produces little change. See Fig. 23. If, however, an ordinary acid be mixed with the litmus, a more extensive alteration is effected: the maximum of absorption takes place not in the yellow, but in the bluish green space, about midway between *b* and *F*: the red and orange rays are transmitted with the greatest readiness, the yellow less readily, the green is speedily absorbed, while the blue, indigo, and violet, though faint, penetrate some distance into the liquid. See Fig. 24. The transparency of this solution to the more refrangible part of the spectrum depends

on its degree of acidity; indeed, if very slightly acid, a thin stratum of litmus appears of a light bluish purple.

Salts, each constituent of which is coloured.—When two bodies combine, each of which exerts an influence, and a different influence, on the rays of the spectrum, it might be expected at the first thought that the resulting colour would be the colour of the first constituent, plus the colour of the second constituent; but a moment's reflection will show that this cannot be: the one constituent will absorb certain rays, and the other certain other rays, and the salt itself will transmit only those rays which are not absorbed by either, or in other words, those rays which are transmitted by both. Thus the resulting colour may sometimes to the unaided eye bear no kind of relation to the original colours. As an instance, acid chromate of chromium may be taken. This salt, compounded of two substances which give respectively yellow and green solutions, is not a bright green, but a brownish red: yet this is just what theory requires, as will be evident on noticing the rays not absorbed by either Fig. 1 or 19. And even where the combination of the two substances does give the reputed resultant of the two original colours, as in the chromate of copper (Fig. 9), which is yellowish green, the resulting colour really does not contain the whole of either of the original prominent tints, but is due to the rays that lie between them, and are common to both. Compare Figs. 13 and 19.

This persistence of the chromatic effect of substances with whatever they are combined, renders it sometimes impossible to decide whether two coloured constituents have combined or not; thus, on mixing permanganate of potash with ferric chloride, we still see the very remarkable series of bands that characterizes the first of these solutions (Fig. 12), and the complete absorption of the blue caused by the second (Fig. 6), but there is nothing in this circumstance, either to prove or disprove the formation of permanganate of iron. Nor does the fact that the mixture of the blue permanganate with the yellow ferric salt, has produced a red solution, afford any indication of a chemical change; that colour might be, and indeed was, anticipated from a consideration of what rays were absorbed by each. Indeed, if blue sulphindigotate of potash be mixed with yellow chromate of potash, the resulting colour is likewise red, and not green, although certainly no combination has taken place between them. How easily might a chemist be

mised, and suppose that the unexpected colour indicated the production of a new substance !

This examination of apparent exceptions to the general rule that "all the compounds of a particular base, or acid, have the same effect on the rays of light," shows that, even in these cases, the rule still holds good, or at least that the differences are only modifications of a common type.

The following conclusions, of practical value in analysis may be drawn :

1. When the light transmitted by a coloured solution of unknown composition is examined by a prism, little can be inferred from the fact that a particular ray is absorbed, unless, indeed, we happen to recognize some of those very peculiar black bands which characterize certain bodies, as the permanganates ; but from the fact of a particular ray being transmitted, we may conclude as almost certain that none of those bodies which in ordinary combination absorb that ray, are there present in any kind of combination.

2. Beside this negative inference, we may frequently arrive at a positive conclusion. It is a rare circumstance that the mere colour of a solution will inform even the most experienced eye of what it is that imparts the colour ; but directly it is examined by the hollow wedge and prism, some familiar spectral appearance may be recognized, which cannot be mistaken, and is at once distinctive. Thus, suppose we have an inorganic salt, which gives a green solution : it may be a compound of nickel, or of protoxide of iron or of uranium, of sesquioxide of chromium, or possibly of copper, of ferric oxide, or of the protoxide of molybdenum, or it may be a ferridecyanide, or a compound salt, such as chromate of copper. True, these greens are not all alike to the unaided eye, but the differences of their character are not easily described or remembered ; but let the prism be applied to them, and they are at once distinguished, and that without losing a drop of the solution. The different appearances are represented side by side in the plate, viz. Figs. 1 to 9.

Fig. 1. A salt of sesquioxide of chromium in weak solution. Already described.

Fig. 2. A salt of nickel. A spectrum in which the extreme ends, the red and violet, are soon cut off, while the whole middle portion is transmitted without change.

Fig. 3. A protosalt of iron after being exposed for a short time to the atmosphere. The pale bluish green solution of a pure ferrous salt admits all the rays freely, but the most refrangible are reduced in intensity.

Fig. 4. A protosalt of uranium. These remarkable absorption bands were pointed out first by Stokes.

Fig. 5. Green chloride of copper. Already described.

Fig. 6. Citrate of the sesquioxide of iron in dilute solution. Already described. It differs from the copper salt principally in the constant presence of the red ray.

Fig. 7. Green chloride of molybdenum. Similar to the chloride of copper, but transmitting red for some distance, and a larger amount of blue.

Fig. 8. A ferridcyanide. The potassium-salt (the only one examined) appears green, except in very deep solution, when it is red: the prismatic appearance of thin strata resembles that of citrate of iron, but afterwards absorption takes place of the rays just beyond *D*, and those more refrangible are gradually absorbed afterwards, till at last the rays between *E* and *b* alone penetrate; then these disappear, and the spectrum between *A* and *D* passes onwards alone.

Fig. 9. Chromate of copper. The yellow and green are constantly transmitted; the red and orange are gradually absorbed; the more refrangible half of the spectrum is cut off at once.

These observations will be sufficient to prove that the varying chromatic phenomena exhibited by different substances, may be taken advantage of in qualitative analysis, to an extent which has been hitherto unappreciated. My remarks have been almost confined to transmitted light; but the phenomena of reflected light offer a similar, and as yet almost unoccupied field of investigation. What I have here marked down must be considered rather as a tentative inquiry, than as a really valuable contribution to our knowledge of the effect of different chemical substances on the rays of light; but should any one be induced to take up the matter systematically, he might easily make such a series of observations, as would furnish data for regular tables of comparison, and the prism would then take its place, as the blow-pipe does now, among the recognized and almost indispensable instruments of the analytical laboratory.



PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

January 19, 1857.

Dr. MILLER, President, in the Chair.

The following donations were announced :—

“The Pharmaceutical Journal:” from the Editor.

“The Journal of the Society of Arts:” from the Society.

“Memoirs of the Academy of Sciences of Madrid:” from the Academy.

A paper was read :—

“On the Composition of Wheat Grain and its products in the Mill, with some observations on Bread:” by J. B. Lawes, Esq., and Dr. Gilbert.

February 2, 1857.

Dr. MILLER, President, in the Chair.

The following donations were announced :—

“The Journal of the Society of Arts:” from the Society.

“The Journal of the Photographic Society:” from the Society.

“The Pharmaceutical Journal:” from the Editor.

The following gentlemen were elected Fellows of the Society :—

Cornelius Hanbury, Esq., Plough Court, Lombard Street.

John Jones, Esq., Duffryn Chemical Works, Risca.

Thornton John Herapath, Esq., Bristol.

Francis Thirkill Conington, Esq., C.C.C., Oxford.

Papers were read :—

“On Alum in Bread, and its Detection:” by E. H. Hadow, Esq.

“On the use of the Prism in qualitative Analysis:” by Dr. J. H. Gladstone.

February 16, 1857.

Col. PHILIP YORKE, Vice-President, in the Chair.

The following gentlemen were elected Fellows of the Society:—

Rev. John Barlow, M.A., F.R.S., 5, Berkeley Street.

Thomas William Burr, F.R.A.S., Gresham Villa, Highbury.

Henry Hancock, Jun., Esq., 59, Harley Street.

Papers were read :—

“On the valuation of Nitre,” by Messrs. Abel and Bloxam.

“On the Thermo-electric properties of various Metals in reference to the direction in which Heat and Electricity cross their Joints:” by R. Adie, Esq.

“Note on Crystallized Bin oxide of Tin:” by F. A. Abel, Esq.

“On the temperature of Charcoal while traversed by an Electric Current:” by R. Adie, Esq.

The Chairman declared the names of the Officers and Members of Council who retire from office at the approaching Anniversary Meeting, in accordance with the bye-laws; and of the Officers and Members of Council recommended by the Council for election.

March 2, 1857.

Dr. MILLER, President, in the Chair.

The following donations were announced:—

“The Pharmaceutical Journal:” from the Editor.

“The Journal of the Photographic Society:” from the Society.

“The Proceedings of the Royal Society:” from the Society.

"The London University Calendar:" from the University.

"The Journal of the Franklin Institute:" from the Institute.

"The American Journal of Science and Art:" from the Editors.

Dr. B. Winstone, 7, Ely Place; and

Dr. George Harley, University College, were elected Fellows of the Society; and

Dr. Frederick Dupré, 53, Burton Crescent, was elected an Associate of the Society.

A Discourse was delivered, entitled "A Report on recent Patents connected with the Reduction and Purification of Iron, and its Conversion into Steel:" by F. A. Abel, Esq., Director of the Chemical Establishment of the War Department.

March 16, 1857.

Dr. MILLER, President, in the Chair.

The following donations were announced:—

Dr. Miller's "Elements of Chemistry, Part 3 (Organic Chemistry):" from the author.

"The Journal of the Franklin Institute:" from the Institute.

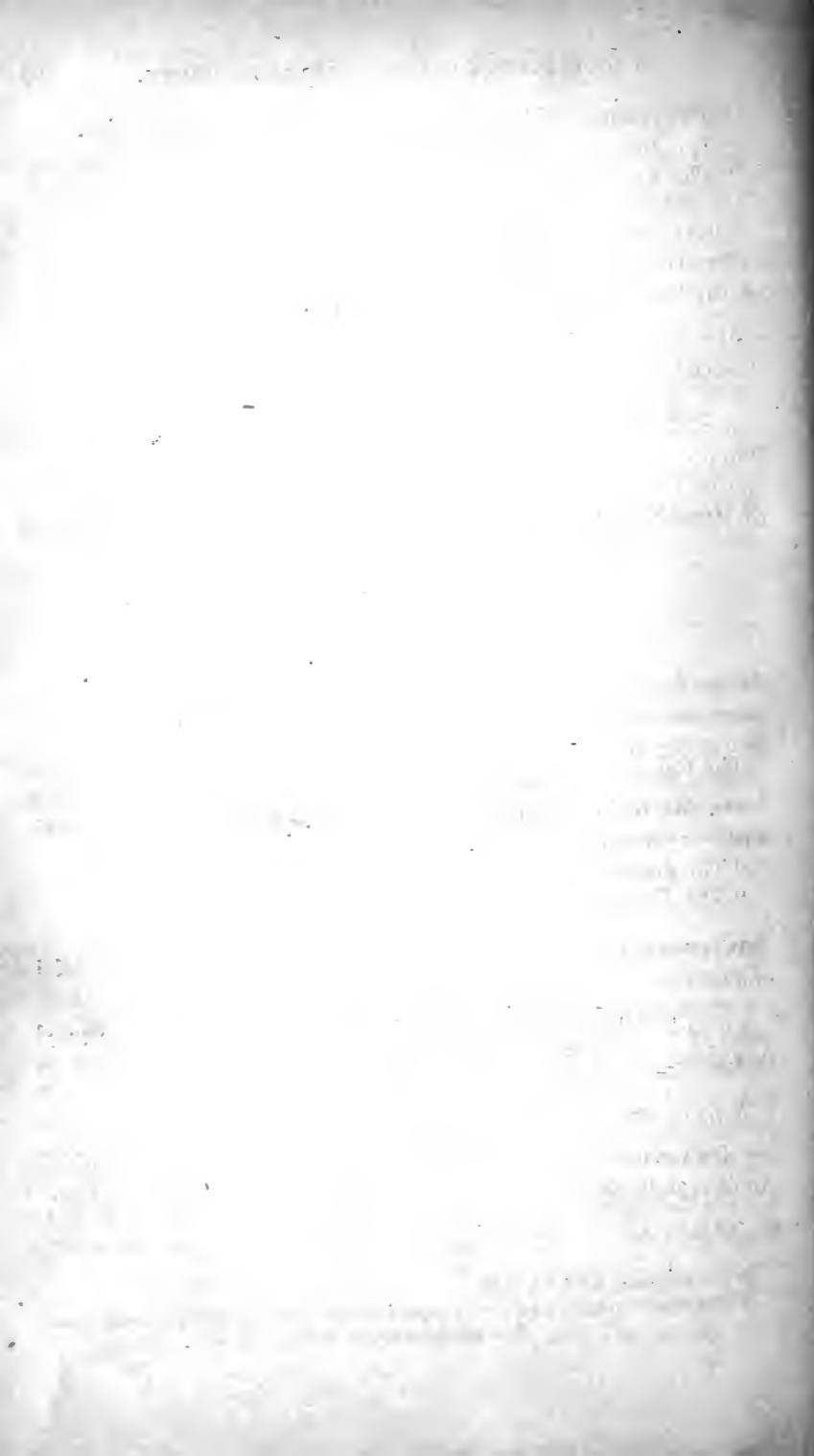
"The Journal of the Society of Arts:" from the Society.

William J. Dent, Esq., was elected a Fellow of the Society; and

John Spiller, Esq., and Edwin O. Brown, Esq., were elected Associates of the Society.

A paper was read:—

"On circumstances tending to disguise the presence of various Acids and Bases in Chemical Analysis:" by John Spiller, Esq.



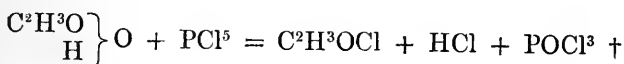
THE
QUARTERLY JOURNAL
OF
THE CHEMICAL SOCIETY.

VII.—*On Compounds obtained by the Action of Anhydrous Sulphuric Acid on the Chlorides of Hydrogen and Ethyl.*

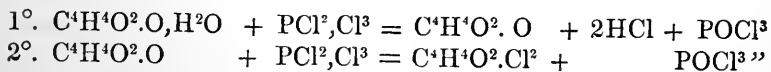
BY ROBERT WILLIAMSON,

OF UNIVERSITY COLLEGE, LONDON.

It has been stated by Gerhardt* that the reaction which takes place between pentachloride of phosphorus and monobasic acids, is not the same as the reaction between the same body and bibasic acids. In the first case, two chlorides are formed, viz., chloride of hydrogen and chloride of the radical of the acid: thus, with acetic acid, the reaction is:



But, according to Gerhardt, the reaction between pentachloride of phosphorus and a bibasic acid consists of two stages. "When, for example, one atom of hydrated succinic acid is treated with one atom of the perchloride, the products are anhydrous succinic acid, hydrochloric acid, and oxychloride of phosphorus; but when anhydrous succinic acid is treated with an additional atom of perchloride, chloride of succinyl and oxychloride of phosphorus are obtained.



* Compt. Rend. XXXVI, 1052.

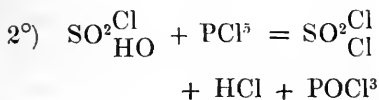
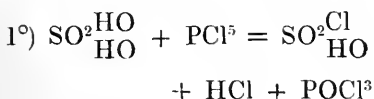
† The atomic weights used in this paper are those proposed by Gerhardt, viz.—
C = 12, S = 32; O = 16;

Similarly, Gerhardt describes the action of pentachloride of phosphorus on hydrated sulphuric acid, or on a sulphate, as consisting, *first*, in the formation of anhydrous sulphuric acid (together with hydrochloric acid and oxychloride of phosphorus.) *Secondly*, in the transformation of this anhydrous sulphuric acid, by another atom of pentachloride, into chlorosulphuric acid.

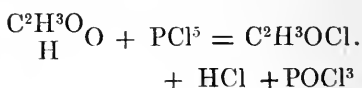
This supposed difference in the behaviour of monobasic and bibasic acids with perchloride of phosphorus, is connected by Gerhardt with the fact, that the atom of a monobasic acid does not contain the quantity of hydrogen requisite for the formation of water, while the atom of a bibasic acid contains the elements of its anhydride with the elements of one atom of water; and he supposes that it is on this atom of water only that the chloride of phosphorus first acts.

This account of the action of pentachloride of phosphorus on the bibasic acids has been shown by Dr. Williamson* to be inaccurate in the case of sulphuric acid. With this acid, the reaction does indeed take place by two stages, but the second is an exact repetition of the first, and each is exactly the same as the one stage of the reaction between chloride of phosphorus and a monobasic acid. For the sake of comparison, the reactions may be written side by side.

Sulphuric acid and chlor. phosphorus.



Acetic acid and chlor. phosphorus.

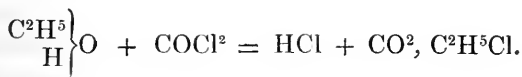


In each case, the change which the hydrated acid undergoes, may be stated, empirically, to be the replacement of an atom of binoxide of hydrogen by an atom of chlorine. And it is evident from the above equations, that this replacement can take place twice in a bibasic acid, but only once in a monobasic acid. The result of the replacement of one atom of binoxide of hydrogen in

* Proc. Roy. Soc. vii. 11.

hydrated sulphuric acid by chlorine, is the compound SO^3ClH , which is strictly intermediate between the hydrated acid and Regnault's chlorosulphuric acid (SO^2Cl^2). The capability of forming such a compound, intermediate between the hydrated acid and the chloride of the acid radical, seems to be a general character distinguishing bibasic from monobasic acids.

It is evident that between a hydrated tribasic acid (PO^4H^3) and its chloride, (POCl^3) *two* intermediate compounds may exist ($\text{PO}^3\text{H}^2\text{Cl}$ and PO^2HCl^2). As examples of bodies similarly constituted to Dr. Williamson's chlorohydrated sulphuric acid, (SO^3HCl), there may be mentioned Chiozza's chlorobenzoic acid ($\text{C}^7\text{H}^5\text{ClO}^2$)* and the substance which Dumas obtained by the reaction of chlorocarbonic acid on alcohol. This body is to chlorocarbonic acid and hydrated carbonic acid, what chlorohydrated sulphuric acid is to chlorosulphuric acid and hydrated sulphuric acid, but contains an atom of ethyl in place of an atom of hydrogen. Its formation is represented by :

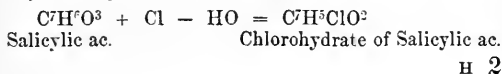


Chlorohydrated sulphuric acid is formed, not only by the action of perchloride of phosphorus on hydrated sulphuric acid but by the action of chloride of sulphur and chlorine on sulphuric acid, by the action of chlorine on sulphurous acid in presence of moisture, in contact with platinum black at a red heat, and by the combination of hydrochloric acid with anhydrous sulphuric acid.

The present paper contains an analysis of chlorohydrated sulphuric acid obtained by the last process, and also an account of compounds similarly obtained from the chlorides of ethyl and methyl and anhydrous sulphuric acid.

Chlorohydrated Sulphuric Acid, SO^3ClH .—This substance was prepared by saturating anhydrous sulphuric acid with hydrochloric acid which had been dried by anhydrous phosphoric acid. The compound so formed agreed in all its properties with the chloro-

* This substance has been found by Mr. Lockwood, of this laboratory, to give salicylate of potash, and not chlorobenzoate of potash, when boiled with alcoholic potash. It is, therefore, chlorohydrated salicylic acid :



hydrated acid described by Dr. Williamson* as obtained from pentachloride of phosphorus and hydrated sulphuric acid.

The composition of chlorohydrated sulphuric acid was determined by decomposing a portion of it with water, and estimating the sulphuric and hydrochloric acids formed. This was done by neutralising the aqueous solution with baryta-water, and, after filtration from the sulphate of baryta, precipitating the hydrochloric acid as chloride of silver. Two experiments of this kind gave .7487 grm. sulphate of baryta to .4353 grm. chloride of silver, and .6887 grm. Ba^2SO^4 to .4189 Ag Cl. These results correspond with the percentages:

| | I. | II. | Cal. (SO^3HCl) |
|---------------------|---------|---------|----------------------------------|
| SO^3 . . . | 69.87 . | 68.93 . | . 68.67 |
| HCl . . . | 30.13 . | 31.08 . | . 31.33 |

The process by which I obtained chlorohydrated sulphuric acid is similar to that by which Rose† obtained compounds of anhydrous sulphuric acid with the chlorides of ammonium, potassium, and sodium. Chlorohydrated sulphuric acid is, in fact, the acid of which Rose's compounds are the ammonium, potassium, and sodium salts; and is probably identical with the compound which Rose obtained‡ by the action of anhydrous sulphuric acid (or better, of Nordhausen acid) on chloride of sulphur.

Chlorosulphate of Ethyl $\text{SO}^3\text{C}^2\text{H}^5\text{Cl}$.—This substance was obtained by the direct combination of chloride of ethyl with anhydrous sulphuric acid. Its composition was determined by finding the weight of the product obtained by combining a known weight of SO^3 with chloride of ethyl.

The experiment was conducted in the following manner. A

* In the notice of chlorohydrated sulphuric acid published by Professor Williamson, that substance is described as distilling without alteration at 145°C .; but I am informed by him that he afterwards found that by long boiling it is partially decomposed; so that if a portion of chlorohydrated acid which has been distilled upwards for some time is distilled with a thermometer, chlorosulphuric acid distils first, then unaltered chlorohydrated, and, lastly, hydrated sulphuric acid. If the middle part of the distillate is again submitted to the same treatment, a fresh portion of chlorosulphuric and hydrated sulphuric acids may be obtained. By repeating this process, a given quantity of chlorohydrated sulphuric acid may be resolved almost completely into chloro-sulphuric and hydrated sulphuric acids. The decomposition which takes place is:



† Pogg. Ann. XXXVIII. 117.

‡ Pogg. Ann. XLIV. 291, and XLVI. 177.

bottle containing anhydrous sulphuric acid was provided with a perforated stopper, to which was fused a horizontal glass tube about 2 feet in length, and $\frac{3}{8}$ in. in diameter. This tube was drawn out before the blow-pipe at intervals along its whole length so as to form a series of narrow bulbs from 2 to 3 inches long, connected by pieces of almost capillary tubing. This series of bulbs being connected with the bottle of anhydrous acid by the perforated stopper, the bottle was warmed, and the acid condensed in the further bulb by cooling it in a mixture of ice and salt. The freezing mixture was moved from one bulb to the next, going towards the acid bottle as each one became full of the acid. When all were filled, the two ends of the tube were fused, and the bulbs separated from one another.

One of these bulbs of acid was weighed, and sealed up in a glass tube with chloride of ethyl. The bulb was broken by shaking the tube, and when the acid was dissolved, the excess of chloride of ethyl was distilled off at about 15°C . When the product ceased to lose weight, the weight of the tube in which it was contained was ascertained, and also that of the bulb which had held the sulphuric acid. In this way the following results were obtained :

| | | |
|------|--------------------|--------|
| I. | weight of compound | 7.5866 |
| II. | | 7.4757 |
| III. | | 7.3776 |

Anhydrous acid used 4.1424 grammes.

| | Found | | | Calc. |
|---------------------------------|---------|--------|-------|-------|
| | I. | II. | III. | |
| SO_3 | 54.601, | 55.41, | 56.14 | 55.36 |
| $\text{C}_2\text{H}_5\text{Cl}$ | 45.399, | 44.59, | 43.86 | 44.63 |

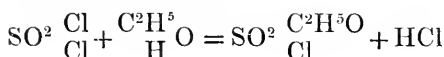
From these weighings it would appear that, at the first, a little chloride of ethyl remained with the sulphuric acid compound, and, in the last, some of the chloro-ethylated sulphuric acid had distilled over.

The pure compound is a colourless oily liquid, heavier than water, at the bottom of which it will lie for weeks without thoroughly decomposing. Sulphuric and hydrochloric acids may, however, be detected immediately after its immersion, and, on neutralising the liquid with baryta, a soluble salt is formed, which I believe to be sulphovinate of baryta.

The compound has a peculiar, sharp, pungent smell. When dry ammonia is passed into it, part of it is precipitated as a white solid body, and, if water is now added, it emits a nutty odour; the solution forms a soluble barium-salt.

A similar compound is formed with chloride of methyl, but could not be satisfactorily examined, on account of the difficulty of condensing the chloride.

I have since formed a body smelling exactly like the ethyl-compound by adding absolute alcohol to chloro-sulphuric acid. The action is probably as follows :



I have also tried the action of chloride of ethyl, $\text{C}_2\text{H}_5\text{OCl}$, on anhydrous sulphuric acid. It dissolves the acid very rapidly, with evolution of heat, and forms a colourless compound, which afterwards turns yellow and then red, even while sealed up. It is rapidly decomposed on opening the tube; and from this cause I was precluded from determining its composition.

When dropped into water, it sinks to the bottom and gradually dissolves, forming an acid liquid. This liquid forms with baryta a soluble salt, which yields a gelatinous precipitate on the addition of an alkali.

VIII.—On a Compound obtained by the Action of Fuming Sulphuric Acid on Chloride of Phenyl.

BY L. HUTCHINGS,

OF UNIVERSITY COLLEGE, LONDON.

By the action of fuming sulphuric acid on benzin (hydride of phenyl), Mitscherlich* obtained sulphobenzidic acid, $\text{C}^6\text{H}^6\text{SO}^3$. The substance described in the present paper was obtained in a similar manner from chloride of phenyl.

The chloride of phenyl employed was prepared from hydrate of phenyl and pentachloride of phosphorus, as described by Mr. Scrugham.†

* Pogg. Ann. XXXI. 283.

† Chem. Soc. Qu. J. vii. 238.

When fuming sulphuric acid and chloride of phenyl are brought in contact at the common temperature, they gradually combine; and, on treating the resulting liquid with excess of milk of lime, a soluble lime salt is obtained, which crystallises, on evaporation, in flat tabular crystals.

0.259 grm. of this lime salt gave 0.06 grm. carbonate of lime, containing 0.024 grm. calcium = 9.26 per cent.

0.2744 grm. of this lime-salt gave 0.3044 grm. sulphate of baryta, containing 0.042 sulphur = 15.22 per cent.

These quantities agree with the formula $C^6H^4Cl Ca SO^3^*$

| | Calc. | Found. |
|----------------|-------|--------|
| 6 C . . . 72.0 | 34.03 | |
| 4 H . . . 4.0 | 1.92 | |
| Cl . . . 35.5 | 16.78 | |
| Ca . . . 20.0 | 9.46 | 9.26 |
| S . . . 32.0 | 15.13 | 15.22 |
| 3 O . . . 48.0 | 22.68 | |

| | | |
|--------------------|-------|--------|
| $C^6H^4Ca Cl OS^3$ | 211.5 | 100.00 |
|--------------------|-------|--------|

The acid may be regarded as a compound of anhydrous sulphuric acid with chloride of phenyl.

IX.—Notes on Alum in Bread and its Detection.

BY EDWARD ASH HADOW,

DEMONSTRATOR OF CHEMISTRY IN KING'S COLLEGE, LONDON.

THERE are two methods recommended in chemical works, with a view to the detection of alum in bread, to both of which there appear at first sight to be theoretical objections, rendering it difficult to understand how they could answer the purpose for which they were proposed. One method, that of Messrs. Robine and Parisot, depends on the extraction of the alum from the bread by digestion in cold water, and then testing the clear filtrate for sulphuric acid and alumina, with chloride of barium and ammonia respectively. This method seems open to the objections that the detection of sulphuric acid would not prove much, since it might have been derived from the common salt employed in making the bread; and the non-precipitation of alumina would not make its

* C = 12; S = 32; O = 16.

absence certain, since it might be retained in solution by organic matters extracted from the bread. The second method, that recommended by Kuhlman, consists in incinerating the bread, digesting the ash in nitric acid, and after filtration, testing the filtrate for alumina with potash; here again it seems questionable whether the alumina would be found capable of solution in nitric acid after the prolonged incineration of the bread.

With a view to settle these points, 20 grains of alum were given to a baker to be introduced into a 1lb. loaf of bread, which being in the proportion of 80 grains to the quartern loaf, is probably above the average amount employed; the loaf thus prepared was broken up and macerated in successive portions of water for 48 hours. The expressed liquids mixed, became perfectly clear by filtration through coarse paper. The filtered liquid was very feebly acid to litmus paper, rendering it by long immersion purple rather than red. One portion tested with chloride of barium, the other with ammonia, gave moderate precipitates. The great bulk of the liquid was evaporated to dryness, and ignited to get rid of a quantity of gummy organic matter. The residue, which fused readily, owing to the common salt present, dissolved for the most part in water, and wholly on the addition of a little nitric acid. Potash (pure and free from alumina) gave on addition an abundant precipitate insoluble in excess, and the filtrate remained perfectly transparent on addition of excess of chloride of ammonium, proving thus the total absence of alumina. The inorganic matters extracted by water were further examined, and found, in addition to common salt and sulphate of potash, to contain alkaline phosphates existing in the fused ash, at first as pyrophosphates, together with phosphate of lime, and a large quantity of phosphate of magnesia, which fully accounts for the precipitate obtained by ammonia in infusion of bread.

The glutinous mass of the bread left undissolved by water, was then incinerated completely, when the ash was found to be wholly soluble in dilute nitric acid. Potash was then added in excess, and the whole was filtered on testing the solution with chloride of ammonium; alumina was found in abundance; the portion of the ash insoluble in potash was chiefly phosphate of iron and manganese with a little phosphate of lime. Thus, it appears, that on treating alumed bread with water, no alumina is extracted even when alum is present in so large a proportion, so far from it, that the aqueous infusion of this bread produced an immediate precipi-

tate with a solution of alum, becoming abundant on gently warming the mixture, and rendering it impossible that alum should exist in the solution, so that this process of maceration in water only, is entirely fallacious, and any sample of bread thus examined will give a precipitate with ammonia; but this precipitate consists only of phosphate of lime and phosphate of magnesia and ammonia, the extraction of which by water only, appears somewhat remarkable, the acidity of the liquid being insufficient to account for their solution. The removal of these phosphates by water appears to be nearly complete, while the retention of alumina and phosphates of iron and manganese is no less entire.

The quantity of alkaline phosphates present in the ash, renders it highly probable that the alumina is retained as phosphate, which would sufficiently account for its ready solubility in nitric acid, after strong ignition; at any rate Kuhlman's method of extraction by nitric acid from the ash answers perfectly, the only objection being the length of time required for complete incineration of the bread, to obviate which, it may, after charring in a capsule of platinum, be deflagrated with nitrate of potash, a process which can be effected over a spirit lamp. On digesting the mass in water, the alumina is almost wholly found in solution in the carbonate of potash thus produced.

Nitrate of cobalt is of no use as a means of detecting alumina in the ash, since the phosphates present are capable of giving the same reaction with this reagent before the blowpipe.

Since alumina is thus obstinately retained by bread, it seemed probable that its mordant properties might serve for its summary detection. With this view, a proportion of pure bread was immersed, simultaneously with a piece known to contain alum, in a freshly prepared and dilute decoction of logwood, and set aside for some hours, when a distinct difference between the two pieces was perceptible both in intensity and in shade of colour, which was more evident on breaking the two pieces. The pure bread was simply stained superficially with the pale orange-red colour of the decoction, while the alumed piece had acquired a purple dye, which had penetrated to some depth. A baker, in whose bread alum had been detected, acknowledged the fact when accused of it, but stated that he *only* used 1oz. for a bushel of flour, or 1oz. to about 19 quartern loaves, which amounts to about 5·7 grains of alum per 11b. of bread. Dr. Normandy also states that no effect is produced in improving the appearance of the bread, if the quan-

tity of alum be reduced below 1 in 906 of flour, or below 1oz. per bushel; hence this may be taken as the *minimum* probably in which this ingredient would be added. A loaf was therefore prepared with this proportion of alum, and was found to give a perfectly satisfactory reaction with the decoction of logwood, a piece of pure bread having been immersed at the same time by way of comparison.

Sulphate of zinc was on one occasion detected in bread by Professor Bloxam, when he was led to suspect it, from observing that the ash had a yellow colour while hot, which disappeared on cooling. It is probable that with bread of pure wheat-flour, this phenomenon would not be observed, in consequence of the transformation of the sulphate into phosphate of zinc, by the alkaline phosphates present, there being no excess of alkali present to prevent such a combination. On one or two occasions, however, I have observed a strongly alkaline reaction of the ash, due in all probability to the addition of potatoes; in such a case only would such a phenomenon probably be observed.

Having on one or two occasions detected small quantities of copper in brown bread, and finding it left in the bread after digestion of the latter in water, I wished to try whether sulphate of copper was in the same predicament as alum, and if so, whether ferrocyanide of potassium was capable of detecting its presence, as it is stated to do, by merely moistening the bread with its solution. A loaf was, therefore, prepared with the addition of this salt, in proportion of 10 grains to the lb.; it was macerated in successive portions of water, in which very little copper was found to be dissolved, yet the residue from which all soluble matters had been extracted acquired a decided reddish tint when treated with ferrocyanide of potassium, which was found to produce a more marked effect than ammonia or hydrosulphate of ammonia. Bread thus adulterated, becomes equally with alumed bread, strongly dyed by an infusion of logwood, so that this test, though alone incapable of distinguishing between the two, would at least indicate that something was wrong. In applying this test, the solution should be freshly prepared, and diluted considerably; the pieces of bread should likewise be allowed to float in the liquid for about 12 hours, the effect being more marked than when they are entirely immersed so as to exclude the air. It is possible that unfermented bread might occasionally give a fallacious indication, if the carbonate of soda used were not wholly neutralized by the hydrochloric acid,

added for the purpose, by the baker; as, however, the alkali would pass into the solution, it seems probable that the latter would likewise be simultaneously affected, and the alkaline reaction of the bread would explain the phenomenon. The only unfermented bread thus examined became unmistakeably dyed; the bread, however, had a feebly acid reaction, and was found to contain abundance of alum.

Before concluding, it may be well to remark, that it is difficult to judge of the quantity of alumina present, merely by observing its bulk and appearance on precipitation, since its appearance varies much with its mode of precipitation. It probably appears most abundant when precipitated from its solution in potash by careful neutralization of the latter with a diluted acid, or by the addition of chloride of ammonium and gentle warming; if however, the latter be boiled, or the precipitation be effected by addition of ammonia to its acid solution, the alumina is far more transparent, and in a hasty examination might even be overlooked, when present in small quantity. The decoction of logwood should also be made with water containing carbonate of lime, such as that ordinarily supplied in London; for with a decoction of logwood in distilled water the differences of colour are far less marked.

X.—*On the Valuation of Nitre.*

By F. A. ABEL, and C. L. BLOXAM.

IN accordance with a promise made by the authors at the conclusion of a former paper upon this subject,* they beg to lay before the society the results of the application of their modification of the method of Gay-Lussac, for determining the value of specimens of the commercial salt.

It will be remembered that the modification alluded to, consisted in the substitution of resin for charcoal in the conversion of the nitre into carbonate of potassa, and in the subsequent treatment of the fused mass with chlorate of potassa in order to oxidise the cyanate of potassa, and to obviate the error arising from the reduction of the sulphates.

The following results were obtained in 53 consecutive experiments conducted in this manner.

Mean of 53 experiments upon pure nitre; 99·7 per cent.

* Chem. Soc. Qu. J., ix, 97.

Of these results, 25 exhibited a slight deficiency in the amount of nitre indicated by the standard acid ;

Mean of these 25 experiments . . . 98·7 per cent.

Mean of the remainder . . . 100·7 „

Moreover, a difference, amounting to 0·3 or 0·5 per cent. was observed in the results, according as the strength of the acid employed had been determined by means of pure nitre, or of its equivalent of carbonate of soda, proving that the process was not yet theoretically correct, or the results would have coincided in the two cases.

The alteration of the quantity of resin and of the temperature employed to effect the deflagration, was not found to improve the results.

On examining the mass obtained by the deflagration, the carbon was usually found collected into large flocks, and, therefore, unequally disseminated ; and on examining the residues in such cases, traces of undecomposed nitre were frequently detected.

In the course of subsequent experiments, it was noticed that the decomposition of the nitre appeared to be more complete when the carbon was added in the form of the pure, ignited, finely divided graphite prepared by the recently patented process of Mr. Brodie.

Attention may be called to the circumstance that no cyanate of potassa was to be found in the deflagrated mass when the graphite had been used, while it may be remembered that considerable quantities of this salt were formed when other varieties of carbonaceous matter, which contained hydrogen, were employed, rendering it probable that the ammonia which was always evolved in such cases, is the proximate cause of the formation of cyanogen. The use of chlorate of potassa, however, is still necessary in the examination of samples of nitre containing sulphates.

Twenty grains of pure nitre were mixed with 5 grains of ignited graphite and 80 grains of salt ; after deflagration, the amount of carbonate of potassa formed was determined as usual.

Considerable influence was exerted upon the success of the process, by the degree of heat employed in conducting the deflagration ; if the platinum crucible be heated to moderate redness in a muffle, from 8 to 10 minutes will suffice to complete the decomposition of the nitre, a result which may also be attained, when a gauze burner is used, by prolonging the application of heat for 20 minutes, and covering the crucible with a jacket. If too high a temperature be applied in the muffle, the results always exhibit

a deficiency; the heat should not be sufficient to volatilise the common salt to any considerable extent.

Six experiments made with the above proportions gave, as a mean result, 99·98 per cent. of nitre.

Eleven experiments upon a mixture containing 95 nitre, 2·5 common salt, and 2·5 sulphate of potassa, gave a mean of 94·88 per cent. of nitre.

In treating the fused mass with chlorate of potassa, the crucible was removed from the muffle, the chlorate sprinkled over the surface, and heat applied by means of an argand burner as long as any effervescence was observed. The fused mass was then thrown upon a filter (having been loosened by pouring a little water into the crucible), and washed with hot water till the washings were no longer alkaline.

In the course of the experiments upon pure nitre, a fresh sample of graphite happened to be employed, and the results then fell somewhat short of the theoretical numbers; on enquiry, this was found to be due to the presence of sulphide of iron in the specimen of graphite; after this had been removed by treatment with hydrochloric acid, correct results were again obtained.

The subjoined table exhibits the results of a number of determinations of the value of commercial saltpetre by the graphite process, the amount of nitre thus indicated being compared with that indirectly obtained by determining the various impurities in the sample. The greater number of these analyses were performed by Messrs. Dent and Brown.

Saltpetre employed for each determination 20 grains.

| No. | Nitre obtained | | No. | Nitre obtained | |
|-----|----------------|-------------|-----|----------------|-------------|
| | Directly. | Indirectly. | | Directly. | Indirectly. |
| 1 | 94·85 | 94·81 | 14 | 98·45 | 98·33 |
| 2 | 98·25 | 98·31 | 15 | 98·65 | 98·60 |
| 3 | 98·45 | 98·10 | 16 | 96·05 | 96·00 |
| 4 | 95·85 | 95·79 | 17 | 94·00 | 93·91 |
| 5 | 98·10 | 97·96 | 18 | 98·75 | 98·43 |
| 6 | 96·70 | 96·88 | 19 | 99·50 | 99·72 |
| 7 | 96·90 | 96·73 | 20 | 99·35 | 99·49 |
| 8 | 95·25 | 95·03 | 21 | 94·85 | 94·66 |
| 9 | 95·05 | 95·24 | 22 | 95·35 | 95·27 |
| 10 | 97·10 | 97·41 | 23 | 96·05 | 96·18 |
| 11 | 99·15 | 99·21 | 24 | 95·00 | 95·05 |
| 12 | 93·80 | 94·09 | 25 | 97·10 | 97·32 |
| 13 | 95·35 | 95·43 | 26 | 97·10 | 96·90 |

XI.—*On some remarkable Circumstances tending to disguise the Presence of various Acids and Bases in Chemical Analysis.*

By JOHN SPILLER,

ASSISTANT IN THE CHEMICAL ESTABLISHMENT OF THE WAR DEPARTMENT.

ON commencing a series of analyses of iron ores, under the direction of Mr. Abel, I had occasion to make a number of experiments in the endeavour to obtain a more perfect and rapid method than those hitherto employed, of separating phosphoric acid from alumina.

In the course of this investigation, I was incidentally led to bring together, in the same solution, alum, citric acid, phosphate of soda, and ammonia, the citric acid being added in order to retain in solution the alumina and phosphate of alumina. On attempting to precipitate the phosphoric acid as phosphate of baryta, I was astonished to find that no precipitate was produced, and on considering that there was present in the solution, not only phosphoric acid, but also sulphuric acid from the sulphate of alumina, I was naturally led to inquire further into the cause of sulphuric acid and baryta existing together in the same solution.

Since it was evident that this extraordinary result could only be due to the presence of citric acid, a series of experiments were instituted, in order to determine the influence which citric acid exerts on the formation of precipitates in chemical analysis, the results of which I will now proceed to describe.

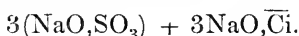
In order to ascertain the conditions under which the precipitation of sulphate of baryta may be prevented by citric acid and the citrates, sulphate of soda was taken as the source of sulphuric acid, and nitrate of baryta as a convenient salt of that base.

To a mixed solution of sulphate and citrate of soda a small quantity of nitrate of baryta was added; the result was, the formation of a bulky white precipitate of citrate of baryta, which immediately redissolved to a clear solution on agitation. On continuing the addition of successive portions of nitrate of baryta, a point was at last arrived at, when a permanent precipitate of sulphate of baryta made its appearance.

In the next experiment, the object was to ascertain the extent to which citrate of soda will prevent the precipitation of sulphate of baryta, and, for this purpose, weighed quantities of each of the substances were employed.

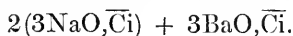
To a known quantity of citrate of soda, sulphate of soda was gradually added, until, on testing a portion of the mixture, the sulphuric acid was immediately indicated by a drop of solution of nitrate of baryta; and it was found that this point was attained when the equivalents of citric acid to sulphuric acid were in the relation of 1 : 3.

In order to confirm this result, equal weights of carbonate of soda were saturated, the one with sulphuric acid, the other with citric acid; on mixing these the salts in solution consisted of



In such a solution, nitrate of baryta gave no permanent precipitate, but on increasing the proportion of the sulphate of soda, the sulphuric acid was immediately rendered apparent.

With a view to determine whether citric acid exercises a similar protective action over baryta, as it does over sulphuric acid, the experiment was reversed, and the citrate of soda added to the salt of baryta. To a known quantity of citrate of soda, nitrate of baryta was added, until a permanent precipitate of citrate of baryta was formed; the solution at this stage containing



On adding a little sulphate of soda, an immediate precipitate of sulphate of baryta was produced.

In connexion with this experiment, it may be stated, that the solution of the double citrate of baryta and soda deposited nearly the whole of the citrate of baryta on standing.

It would appear, therefore, that the protective action is on the side of the acid rather than that of the base.

The conditions under which the precipitate of sulphate of baryta is produced, in a solution made according to the first experiment, are the following:—by boiling, when sulphate of baryta is immediately precipitated; by the addition of an excess of nitrate of baryta; by the addition of hydrochloric, acetic, tartaric, or oxalic acid. The sulphate of baryta, when precipitated from solution by either of these agents, is in a peculiar flocculent condition, totally dissimilar in appearance from that obtained under ordinary circumstances; so finely divided is it, that it readily passes through a filter of Swedish paper. Prolonged boiling, with or without hydrochloric acid, has little effect in changing its physical character.

Citric acid itself has no effect in preventing the precipitation of sulphuric acid by a salt of baryta; and this is probably the reason why the addition of acids to a solution containing a neutral citrate is immediately followed by a precipitation of sulphate of baryta.

These results having been obtained by the use of a baryta salt, it became interesting to know whether the sulphates of strontia and lead were, in like manner, prevented from precipitation by citrate of soda.

To a mixture of sulphate and citrate of soda, nitrate of strontia was added, when no indication of sulphuric acid was observed, the salt of strontia behaving in a precisely similar manner to that of baryta under the same circumstances.

Nitrate of lead substituted for the baryta or strontia in these experiments gave the same result, no sulphate of lead being produced. But sulphate of lead differs from the sulphates of baryta and strontia, in being soluble, after precipitation, in citrate of soda.

My attention was next directed to the power which the citrates possess in influencing the general reactions which characterize the acids and bases in the ordinary course of chemical analysis.

Baryta.—Of the compounds of baryta there is not one that is precipitated when the acid is previously combined with citrate of soda, whether the reaction of the solution be acid or alkaline. The salts of this base, which have been made the subject of experiment, are, besides the sulphate, the phosphate, carbonate, borate, oxalate, tartrate, citrate, and fluoride. With the exception of the sulphate, all these compounds, after precipitation, are again dissolved in neutral citrate of soda.

Strontia.—The acids which were tried in connexion with this base were sulphuric, phosphoric, and carbonic, all of which compounds were retained in solution.

Lime.—Of the lime salts, the carbonate, phosphate, and oxalate were found to follow the general rule, both with respect to prevention of precipitation, and in being redissolved in citrate of soda if once produced.

The fact of oxalate and phosphate of lime being soluble in citrate of soda, suggests the possibility of this salt being employed with advantage in diseases arising from the formation of these descriptions of calculi.

As lime is the reagent generally recommended for the detection of citric acid, it is important to bear in mind that the citrate of

lime will not be thrown down on boiling, unless the chloride of calcium be added in sufficient quantity to decompose the greater portion of the alkaline citrate, since the double citrate of lime and soda does not give any precipitate on boiling.

Magnesia.—The salts of this base appear to be less affected by the presence of citrate of soda, hydrate of magnesia and the ammonio-phosphate of magnesia being precipitated as usual. The phosphate and carbonate are, however, held in solution.

The next group, consisting of the sesquioxides of iron, chromium, and aluminium, are not precipitated by their usual group-test—ammonia. The phosphates of these oxides are also retained in solution by citrate of soda.

Chromium, in the state of chromic acid, is not detected by lead, silver, bismuth, or baryta. The chromate of lead does not even appear on the addition of acetic acid.

Sesquioxide of Iron.—A solution of sesquichloride of iron is not precipitated by ferrocyanide of potassium, benzoate, or succinate of ammonia; nor is the coloured reaction produced with acetate of potassa, ferricyanide, or sulphocyanide of potassium. The reaction between sesquichloride of iron and ferrocyanide of potassium is curiously modified. On mixing these two solutions in the presence of an alkaline citrate, a yellow solution is formed, which becomes deep blue in colour on largely increasing the amount of ferrocyanide of potassium; no precipitate of Prussian blue is produced until hydrochloric acid in excess is added.

From the fact that a salt of iron does not precipitate benzoic and succinic acids in presence of a citrate, the detection of these acids becomes exceedingly difficult, as we are not able to avail ourselves of any of the methods previously adopted for the decomposition of the citrate.

The group comprehending the protoxides of iron, manganese, nickel, cobalt, and zinc, are variously affected by their group-test—sulphide of ammonium. The sulphides of nickel, cobalt, and zinc are precipitated as usual; sulphide of iron incompletely; and sulphide of manganese not at all.

Protoxide of Iron.—Neither potassa nor ammonia will precipitate this base in the presence of citric acid. The alkaline product so obtained gives, with sulphide of ammonium, if dilute, a dark olive-green solution, but if more concentrated, an immediate precipitate, with a supernatant liquid of that colour. The sulphide of iron comes down, however, on boiling, or on standing for a

sufficient length of time in the cold. The protophosphate of iron is held in solution, and the reaction between ferricyanide of potassium and a protosalt of iron is entirely masked.

Oxide of Manganese.—The most striking result observed under this head relates to the behaviour of the sulphide. The flesh-coloured precipitate usually obtained on adding sulphide of ammonium to a salt of manganese, does not appear under these circumstances, and the sulphide, after precipitation, is freely soluble in an alkaline citrate. If citrate of ammonia be the solvent employed, vapour of sulphide of ammonium is evolved on boiling. The protoxide of manganese is not precipitated by potassa, nor the carbonate by carbonate of soda, in presence of a soluble citrate. On exposure to air, the brown binocide of manganese separates from the former only of these solutions.

Oxide of Nickel.—A salt of nickel gives, with sulphide of ammonium, the ordinary black precipitate of sulphide of nickel; but the other reagents, as potassa, carbonate of soda, and ferrocyanide of potassium, fail to give their usual indications.

Oxide of Cobalt.—Solutions of this metal behave in a similar manner to those of nickel, with the several reagents just mentioned. The alkaline solution of protoxide of cobalt in potassa deposits the sesquioxide on exposure to air.

Oxide of Zinc.—This oxide resembles magnesia, in being precipitated by potassa in the presence of a citrate. The carbonate of zinc is retained in solution, but the sulphide and ferrocyanide are not influenced.

Sesquioxide of Uranium.—The phosphate and ferrocyanide of uranium are not precipitated in the presence of citrate of soda.

The metals of the sulphuretted hydrogen group are, with the exception of arsenic, precipitated as usual by their group-test. Several of their principal reactions are completely disguised, as will appear on describing these metals individually.

Oxide of Lead.—Besides the oxide itself, the sulphate, phosphate, carbonate, and oxalate, the bromide, iodide, cyanide, and ferrocyanide are all retained in solution on the addition of their respective precipitants. The only compound of lead, of those experimented upon, which made its appearance as under the usual circumstances, was the sulphide. The chromate has been already referred to as having its characters completely masked.

Oxide of Silver.—Inasmuch as the nitrate of silver is frequently employed for the detection and discrimination of several acids,

both organic and inorganic, it was thought advisable to make a careful study of the more important compounds of this metal, and to trace their connexion with the ordinary process of analysis.

Nitrate of silver, if added in small quantity to a solution of neutral citrate of soda, gives rise to a precipitate, which, on agitation, is completely redissolved, but on continuing the addition of the nitrate of silver, a permanent precipitate is at last produced. As this final effect can only result in the destruction of the citrate of soda, and the removal of the citric acid as an insoluble silver-compound, it follows that no interfering influence need be anticipated in the ordinary course of testing for acids.

Among the compounds of silver, insoluble under ordinary circumstances, but which are held in solution through the medium of citrate of soda, are the carbonate, phosphate, oxalate, tartrate, and citrate. On the contrary, the sulphide, chloride, bromide, iodide, ferrocyanide, and sulphocyanide are precipitated as usual. The cyanide of silver is slightly soluble in this reagent, so that in its presence, very dilute hydrocyanic acid is not precipitated by nitrate of silver. Oxide of silver resembles magnesia and oxide of zinc in being thrown down by potassa under all circumstances.

Suboxide of Mercury.—By adding potassa to a salt of this base, in the presence of citric acid, the suboxide of mercury is resolved into protoxide, which remains in solution, and metallic mercury, precipitated in the form of minute grey globules. The chloride bromide, and iodide, corresponding to the suboxide, are precipitated in the usual manner.

Protoxide of Mercury.—The sulphide and iodide are not sensibly influenced in their precipitation; the latter is very sparingly soluble in citrate of soda, so that, in a highly dilute solution, the scarlet iodide does not make its appearance. The oxide and carbonate are retained in solution, and if to either of these alkaline liquids, ammonia, or one of its salts, be added, the white precipitate (chloride and amide of mercury) is immediately thrown down. The fact that oxide of mercury is not precipitated by carbonate of soda in the presence of certain salts, and that, on the addition of any compound of ammonia, an immediate precipitate is produced, is not new. A solution of protochloride of mercury, chloride of sodium, and carbonate of soda has long since been employed by Mr. E. O. Brown, as a test for ammonia; and so delicate is this test, that the slightest trace of ammonia is indicated by an opalescence throughout the liquid.

Teroxide of Bismuth.—Neither this oxide nor the carbonate is precipitated if citric acid be present, nor is the terchloride of bismuth decomposed by water. The sulphide is, however, not appreciably affected.

Oxide of Copper.—This oxide and the carbonate are both retained in solution; the sulphide and ferrocyanide are precipitated in the usual manner.

Oxide of Cadmium.—The carbonate and oxide of this metal are also retained in solution, but not so the sulphide, which is completely precipitated.

Protoxide and Bin oxide of Tin.—Both these oxides may be retained in alkaline solution on the addition of ammonia. The sulphides of tin are completely precipitated as under the ordinary circumstances.

Teroxide of Antimony.—The addition of citric acid prevents the precipitation by water of the terchloride of antimony, but does not interfere with the separation of this metal by sulphuretted hydrogen.

Antimonic Acid.—The precipitation of the pentasulphide of antimony does not appear to be so complete as in the case of the tersulphide; the separation of the last portion was attended with difficulty in some of my experiments.

Arsenious and Arsenic Acids.—The characteristic reactions of arsenic are modified in a remarkable manner. A solution of arsenious acid, to which citric acid or a neutral citrate has been added, is no longer precipitated by sulphuretted hydrogen in the cold or on boiling. The tersulphide of arsenic is also readily soluble in citric acid or a citrate. Hydrochloric acid added to either of these solutions, at once separates the whole of the arsenic.

The pentasulphide imitates the deportment of the tersulphide under the circumstances recorded above.

The arsenites of silver, copper, lime, and baryta, and the arseniates of lead, silver, and baryta, are entirely kept in solution.

From a consideration of the circumstances under which the sulphides of arsenic may be preserved in a soluble form, while the same compounds of tin and antimony are completely precipitated, I have been induced to attempt the analytical separation of these metals by such a process. My experiments have not yet been sufficiently numerous to enable me at the present time to point out the conditions under which their perfect separation may be

accomplished, but I have every reason to believe that a quantitative method may be based upon this principle.

Teroxide of Gold.—The precipitation of the sulphide of gold takes place as under ordinary circumstances, but the reaction with protochloride of tin is modified to the extent of the production of a dingy green precipitate, instead of the brilliant purple of Cassius.

Binoxide of Platinum.—The bisulphide of platinum is precipitated on boiling, but not readily in the cold. The double chloride of platinum and ammonium has an increased tendency to assume a crystalline condition, perhaps on account of its formation being slightly retarded.

Finding citric acid to exert such remarkable solvent powers in many of the instances enumerated, I extended the inquiry to a few substances, where a parallel action might have been expected. With this intention, tartaric and racemic acids, glycerine, and the sugars were selected, and their interfering action in some few cases determined.

Tartaric acid prevents the precipitation of a salt of cobalt by potassa, and, in the form of a neutral tartrate, retains in solution sulphate of lead and the sulphide of manganese; Prussian blue is not formed in its presence; and the precipitation of sulphate of baryta is to a small extent retarded.

Racemic acid also slightly retards the precipitation of sulphate of baryta.

Glycerine has, seemingly, no influence in preventing the precipitation of Prussian blue, sulphide of manganese, or sulphate of baryta.

Under the head of the sugars, the only circumstance met with worthy of record, was the power of grape-sugar to prevent, in the cold, the formation of sulphide of manganese. Neither cane nor milk-sugar appeared to have any influence in this direction.

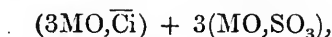
These examples fully confirm the fact long known, that many kinds of organic matter exert a very considerable influence on the formation of precipitates in analytical chemistry, and suggest the necessity of eliminating all these interfering circumstances before testing for the inorganic bases. It is, then, good policy to carry out the instructions of the analytical tables, when, after treatment of the unknown substance with hydrochloric acid and sulphuretted hydrogen, it is recommended to evaporate the filtrate to dryness and to clear organic matter, before proceeding to search for metals belonging to either of the subsequent groups.

Before concluding the account of my experiments on the properties of citric acid, I cannot refrain from mentioning a difficulty early experienced in the detection of tartaric acid, when mixed with a large proportion of citric acid. So imperfect is the ordinary method of proceeding—that of employing a lime-salt to precipitate, in the cold, the tartaric acid as tartrate of lime—that I think it possible for citric acid to be adulterated with as much as 10 per cent. of tartaric acid, without fear of detection. Desiring to ascertain the purity of the sample with which I worked, my attention was naturally directed to this point. By the following process we are enabled to detect the presence of tartaric acid in cases where the old method would not be successfully employed.

To a concentrated aqueous solution of the acid under examination, acetate of potassa is added, and subsequently strong alcohol to the amount of an equal bulk; on stirring with a glass rod the crystalline bitartrate of potassa separates, time being allowed when small quantities only are suspected. By this means it is possible to detect a much smaller amount of this impurity in citric acid.

The same mode of proceeding may be turned to useful account, if the relation between these two acids be reversed. By first separating the tartaric acid as above, and afterwards evaporating the alcoholic filtrate over a water bath, the citric acid may be detected in the residue, by boiling with excess of chloride of calcium in the usual manner.

For the explanation of these curious phenomena I am not able to bring forward any hypothesis with the same degree of confidence that I have treated the facts themselves. The only possible way that has suggested itself to my mind, of accounting for the property possessed by citric acid, of retaining in solution substances which, under ordinary circumstances, are insoluble, is to suppose a neutral salt of citric acid to be endowed with the power of combining, on the one hand, with another salt, containing the *acid* of the compound whose formation is prevented, in such a manner as to produce a class of double salts of the general composition:—



in which the term SO_3 is capable of being replaced by CO_2 , CrO_3 , BO_3 , $\overline{\text{O}}$, &c.; or, in the case of PO_5 , a tribasic acid, one equivalent only will be required to take the place of three equivalents of SO_3 .

On the other hand it must be allowed, that an alkaline citrate

has a tendency to combine with the citrate of another *base*, even though this latter compound be of itself but slightly soluble in water. The affinity existing between the two constituents of the double citrate, taken in conjunction with that exerted in the formation of the class of double-salts, just now referred to, might, it is suggested, determine in favour of the non-precipitation of the otherwise insoluble body involved.

The ascertained facts upon which this hypothesis has been principally constructed, may be shortly stated to consist in the power of one equivalent of citric acid to mask the reactions of either three equivalents of sulphuric or carbonic acid, or one equivalent of the tribasic phosphoric acid; while the existence of a class of double citrates, as those of soda with silver, lime, and baryta respectively, has been rendered highly probable in the course of this investigation.

Additional confirmation is also derived from the circumstance that the carbonates of baryta and lead dissolve in a neutral citrate with production of an alkaline liquid, the new metal remaining in solution in the form of a double citrate. And again, the alkaline product of the action of carbonate of soda on a salt of manganese, in presence of citrate of soda, does not deposit binoxide of manganese on exposure to the oxidising influence of the air, while another solution, containing caustic potassa in place of the carbonate, is constantly absorbing oxygen. An analogous instance in the case of cobalt need scarcely be quoted. All these reactions are explicable, in my opinion, on the view advanced; the affinity of carbonic acid for these several bases, though weak, is strengthened by the formation of a citrocarbonate.

XII.—*Note on Crystallised Binoxide of Tin.*

By F. A. ABEL.

IN the bronze gun foundery at Woolwich, it is customary, in cleaning out and examining the furnace employed in preparing the gun-metal, to collect the small quantity of dross or slag found on the hearth, and to subject it to fusion in one of the crucibles used during the day in the preparation of small castings, in order to

recover the metal disseminated through the mass, by allowing it to subside from the liquid slag.

Upon breaking the crucible, to remove the metal obtained in an operation of this kind a short time since, a cavity was discovered in the slag, between it and one portion of the metallic surface, containing a number of long brilliant needles, which appeared to possess a light brown colour. On careful examination, under the microscope, they proved to be striated, four-sided prismatic crystals of a colourless transparent substance, enclosing here and there small particles of metal.

The crystals were very brittle, and so hard as to scratch glass easily. Some of them were carefully selected, so as to be quite free from slag, and submitted to chemical examination. They proved to be perfectly insoluble in acids, and, when fragments of them were fused with carbonate of soda, they remained unaltered for a considerable period. A few of the crystals were finely pulverised, after digestion in nitrohydrochloric acid, and the enclosed metallic particles separated by levigation. The dense white powder thus obtained was readily dissolved by fused carbonate of soda, and proved to consist entirely of binoxide of tin.

When submitted to the highest blowpipe-heat upon a charcoal support, the crystals evinced no symptom of fusion, until, after some time, partial reduction of the metal ensued. Upon exposing the extremity of a crystal in a platinum support for some time to the hottest portion of the blowpipe-flame, it altered in form a little, and, when examined by a lens, was found to have fused slightly to a yellowish transparent glass.

These crystals of binoxide of tin were not only found in the cavity between the metal and the slag, but were distributed over the entire upper surface of the metal, to which they firmly adhered. The appearance of the metallic surface was very peculiar; the metal itself having assumed the form of tufts, which were interlaced with the crystals of binoxide of tin. The latter would seem to have separated from the gun-metal in the crystalline form as the crucible was allowed to cool.

The formation of such crystals as those described does not appear to be a matter of frequent occurrence; although the operation above alluded to (*i. e.*, the collection of the metal from the slag) has long been a customary one, this is the first instance in which the crystals have been observed by those conducting this operation at Woolwich.

Two shell-like specimens of gun-metal, removed about ten years ago from some crevices above the hearth of one of the furnaces in the same foundry, after a cast, have been preserved by the superintendent, because the interior surfaces were found to be covered with crystals, which prove to be similar, though of inferior size, to those above described.

These crystals of binoxide of tin are quite similar to those described by M. Daubrée as obtained by the action of the vapour of water upon bichloride of tin, at a red heat.

XIII.—*On a New Base from the Juice of Flesh.*

BY A. STRECKER.

LIEBIG, in his classical investigation of the juice of flesh, did not, as is well known, make use of any heavy metallic salt to precipitate the substances which he discovered in that liquid; and it was only after he had become acquainted with the properties of creatinine, which he at first obtained by artificial means,—that he demonstrated the existence of that base in flesh-juice by precipitation with chloride of zinc.

As the juice of flesh, in addition to the principles discovered and examined by Liebig, contains a considerable number of bodies hitherto undetermined, which bodies remain in the form of a thick magma, when the mother-liquor of creatinine is evaporated, I endeavoured to isolate some of these constituents by precipitation with different metallic salts, *e. g.*, mercuric chloride, mercuric nitrate, ammonio-chloride of zinc, and acetate of copper. All these salts produced a considerable precipitate, containing, as an essential constituent, a well characterised organic base, which I will provisionally distinguish by the name *Sarcine*.

The most advantageous method of preparing this base is by precipitation with acetate of copper. The mother-liquor of the creatine-crystals was diluted, and mixed with a dilute solution of acetate of copper; a copious precipitate was then produced, which, when decomposed by sulphuretted hydrogen, yielded a substance soluble in water but still coloured. On boiling the solution of this substance with hydrated oxide of lead, the colouring matter was precipitated, together with a small quantity of sarcine; the

greater part of that substance, however, remained in solution, and after the lead had been precipitated by sulphuretted hydrogen, was obtained in the crystalline form by evaporating the liquid.

From a warm saturated solution, sarcine gradually separates, on cooling, in the form of a white, indistinctly crystalline powder, which often covers the sides of the containing vessel with a dense coherent crust. It dissolves in 300 pts. of water at 15° C. and in 78 pts. of boiling water; but requires 900 parts of boiling alcohol to dissolve it. The solutions do not alter the colour of litmus-paper, and have no very characteristic taste. In hydrochloric acid, ammonia, and potash, sarcine dissolves much more readily than in cold water; dilute nitric and sulphuric acid dissolve it less readily; concentrated nitric and sulphuric acid dissolve it abundantly, without colouring or evolution of gas.

The solution of sarcine in boiling concentrated hydrochloric acid, deposits, on cooling, colourless, nacreous, tabular crystals, containing a considerable quantity of hydrochloric acid. The concentrated solution of these crystals mixed with bichloride of platinum, deposits a yellow crystalline platinum-salt, which dissolves readily in warm water, sparingly in cold.

The solution of sarcine in concentrated nitric acid, deposits, on standing, transparent colourless crystals (apparently rhombic octohedrons) of nitrate of sarcine, which, when exposed to the air or moistened with water, become white and opaque, but without alteration of form. The solution of sarcine in concentrated sulphuric acid likewise deposits, on standing, or on addition of alcohol, colourless, needle-shaped crystals of sulphate of sarcine, which crumble to a white powder on addition of water.

Sarcine is therefore a weak base, capable of uniting with acids and forming a platinum double salt; its salts are, however, in great part decomposed by water. When the solution of hydrochlorate of sarcine is repeatedly evaporated to dryness over the water-bath, a residue is at length obtained, free from hydrochloric acid. Sarcine undergoes no alteration when treated with concentrated acids at 100°; even when its solution is mixed with aqua regia and evaporated over the water-bath, the residue consists mainly of unaltered sarcine.

Sarcine, like other weak bases, unites with metallic oxides and salts, not only with the oxides of the heavy metals, but likewise with the alkalis and alkaline earths. Among all these compounds the silver-compound presents the greatest interest, because it is

best adapted for detecting the presence of sarcine and for preparing it in the pure state.

An aqueous solution of sarcine forms, with nitrate of silver, a flocculent precipitate, which does not dissolve on the addition of dilute nitric acid in the cold; to dissolve it completely, the nitric acid must be tolerably strong and at the boiling heat. As the solution cools, the greater part of the salt separates in colourless scaly crystals, so that the filtrate scarcely yields any precipitate on addition of hydrochloric acid. The crystals consist of a compound of sarcine with nitrate of silver. A totally different compound is obtained by precipitating an ammoniacal solution of nitrate of silver with sarcine; the flocculent precipitate, which is quite insoluble in water and ammonia, dries up, like alumina, to a hard mass, on exposure to the air.

Sarcine is precipitated by basic acetate of lead, but only on boiling; also, by an ammoniacal solution of chloride of zinc, by cadmium-salts, by solution of mercuric oxide, by corrosive sublimate, and many other metallic salts. By alkalies, on the other hand, even by baryta, it is dissolved. From its solutions in alkalies it is for the most part reprecipitated by a stream of carbonic acid gas. Its solution in baryta-water, deposits, on addition of a larger quantity of the baryta-solution, transparent, colourless crystals of *sarcine-baryta*.

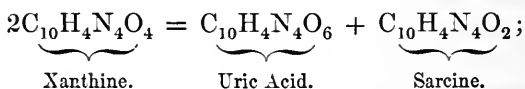
These properties of sarcine would sufficiently show it to be a base, even if its basic character were not decidedly established by the existence of definite compounds with acids, and of a platinum double salt. The bases which it most resembles are *caffèine* and *guanine*; in composition it likewise exhibits a certain analogy to that of these bodies.

The analyses of sarcine and of its compounds lead to the following formulæ:—

| | |
|------------------------------------|--------------------------------|
| Sarcine | $C_{10}H_4N_4O_2$ |
| Hydrochlorate of sarcine . . . | $C_{10}H_4N_4O_2, HCl + 2Aq$ |
| Chloroplatinate | $C_{10}H_4N_4O_2, HCl, PtCl_2$ |
| Sarcine with nitrate of silver . . | $C_{10}H_4N_4O_2, AgO, NO_5$ |
| Sarcine with oxide of silver . . | $C_{10}H_2Ag_2N_4O_2 + 2Aq$ |
| Sarcine with baryta | $C_{10}H_2Ba_2N_4O_2 + 4Aq$ |

Guanine, $C_{10}H_5N_5O_2$ differs from sarcine only by NH , and resembles it closely in its combining relations. Caffeine $C_{16}H_{10}N_4O_4$, contains the same number of equivalents of nitrogen.

Sarcine is identical in composition with *hypoxanthine*, the base which Scherer discovered in the spleen, and traces of which he has since found in the blood. The two bodies likewise agree in certain of their properties, so that I might be disposed to regard them as identical, were it not that Scherer's compound, in respect of its solubility in water, and insolubility in acids, differs from sarcine to an extent which can scarcely be accounted for by difference of purity in the preparation. According to Scherer's statement, hypoxanthine dissolves in warm nitric acid, with evolution of gas, and yields, on cooling, a product of decomposition; and the liquid, when evaporated to dryness, leaves a yellow residue, which assumes a red colour on addition of potash. Sarcine, on the other hand, dissolves in nitric acid, without evolution of gas, and the solution, when evaporated over the water-bath, leaves a *colourless* residue, which does not become yellow till it is strongly heated; on addition of potash, this residue assumes a red colour. This reaction, however, is exhibited by *guanine* and *xanthine* (Marcet's xanthic oxide), as well as by the above-mentioned bodies. Xanthine might, according to its composition, $C_{10}H_4N_4O_4$, be regarded as a compound of uric acid with sarcine:



but its chemical relations, as I have found by experiment, do not accord with such a view of its composition. By mixing a solution of hydrochlorate of sarcine with urate of soda, I have prepared the isomeric compound, *urate of sarcine*. This compound is resolved into its constituents by the action of acids, and in that respect is different from xanthine.

Lastly, I have discovered in human urine a body identical with sarcine, or at all events very closely resembling it. This body forms, with nitrate and with oxide of silver, compounds resembling those formed by sarcine: it may, nevertheless, be not sarcine but guanine—a point to be decided by the analysis which I am about to undertake.

I have as yet used only beef and horse-flesh for the preparation of sarcine, and have obtained it in about equal quantity from both.

XIV.—*Report on Recent Patents connected with the Reduction and Purification of Iron, and the Manufacture of Steel.*

By F. A. ABEL,

DIRECTOR OF THE CHEMICAL ESTABLISHMENT OF THE WAR DEPARTMENT.

THE progress made during the last two or three years in the manufacture of iron, would appear, from a cursory inspection of the patents published within that time, to relate principally to the treatment of the metal, after its elimination from the ore by the agency of the blast furnace, the process of the reduction of iron from its ores having undergone apparently no very important modification since the introduction of the hot blast.

Although the general truth of this may be admitted, it is well known to all who have devoted themselves to a more minute examination into the details of iron manufacture, that many of those actually engaged in directing operations with the blast-furnace have, by a careful study of the relations between the product, the temperature, and blast, the proportions of the materials employed, &c., succeeded in regulating the working of the furnace to such an extent, as, on the one hand, almost to ensure uniformity of product, and on the other, to raise very considerably the quantity of iron yielded by the furnace in a given time.

It is also well known, though less openly acknowledged, that the iron-master has, within the last few years, succeeded in manufacturing a marketable iron from materials which in former times were either considered as useless, or employed only in comparatively small quantities. It is this circumstance which has led, on more than one occasion, to an outcry against the hot-blast process, as having placed within the reach of the iron-master the power of increasing the quantity of his product from the blast-furnace, at the expense of its quality.

While, therefore, the efforts of the iron-master have raised the manufacture of iron in Great Britain to a marvellous height, as regards actual quantity of metal produced, (the annual amount of which is shown, upon competent authority, to equal the *sum* of that furnished by all other iron-making countries), they have at the same time raised within the minds of those who watched these achievements with wonder and pride, the fear, that British iron is in danger of losing the general reputation which it has

possessed for high quality; a fear in great degree nourished by the opportunity afforded in 1855 for an examination of the excellent results of the labours of foreign iron manufacturers.

Abundant evidence has, however, been recently afforded that the quality of iron is a subject not likely to be neglected in England; it has for some time past occupied an unusual share of general public attention; it has been made the subject of ingenious contrivance and scientific research; and at the present time some of our most extensive iron manufacturers are actively engaged in determining, by extensive trials, the merits of some of our more prominent schemes for its improvement.

An attempt has been made in the present report, to fulfil the desire of the Council of the Chemical Society, to present its Fellows with an outline of the improvements in the various processes connected with the reduction and purification of iron, or its conversion into steel, which have been suggested or actually carried out within the last two or three years. In a report of this description, it is impossible to enter into the consideration of improvements in the construction of furnaces, or of the appliances for iron manufacture, excepting in so far as they are concerned in carrying out effectually the chemical principles involved in the various proposals which will have to be referred to.

The difficulties necessarily experienced, even with the best opportunities at command, for collecting information, in the endeavour to give some account of the actual improvements effected in iron-manufacture, are very considerable; emanating as they do, on the one hand, from the impossibility of obtaining trustworthy information as to the full extent to which the numerous proposals made public as patents, have met with successful application; and on the other, from the circumstance that many of the improvements in the ordinary method of iron smelting which furnish beneficial results to the iron-master by whom, or in whose establishment, they have been elaborated, are not published to the world through the Patent Office, or through any other channel. That this should be the case cannot excite surprise; the iron trade, like every other, must have its secrets, jealously guarded by their fortunate owners; moreover, it must be remembered that any peculiarities in the treatment of the ore adopted by a particular iron-master, may have been called forth by the nature of the materials at his command, the locality in which his works are situated, or the class of product which he is most desirous of

manufacturing advantageously. Or, possibly, he may fear that the circumstances constituting to him an important improvement in the system of iron smelting, would, if publicly known, tend to raise a prejudice against the iron which he sends into the market.

Men of science and ingenuity have, however, not been wanting during the last few years, who have made public and secured to themselves the claim to modifications in the present method of iron smelting by the blast-furnace, or to new plans for reducing the metal from its ores. It is but natural that some of the patented processes relating to iron smelting should not be likely to lead to any beneficial results, when put to practical tests; there are many, however, which embrace important principles, and which though, individually, they may not all realise the sanguine expectations of their proprietors, are likely, if classified and studied collectively, to lead to substantial and general improvements in iron smelting. These remarks apply, even with greater force, to the very numerous processes for partially or completely refining iron with economy and success, or for the manufacture of steel or other varieties of iron, which have been patented during the last two or three years. The circumstances that the processes of refining, puddling, and balling, bear no proportion, as regards their rapidity, or the scale upon which they can be conducted, to the process of iron smelting by hot blast, and that, with the greatly increased demand for wrought iron, &c., the treatment of inferior qualities of pig-iron by the refining processes, is frequently a matter of necessity, have combined with numerous other considerations, not only to set at work the inventive faculties of ingenious theorists, but to rivet the attention of men thoroughly acquainted with the intricacies and the requirements of iron manufacture; and as the result of this, it may be fairly asserted that the system of iron refining is, at the present time in a state of transition, and that a proper elaboration of the principles involved in some patented processes, which have of late excited the serious attention of several of our most extensive iron manufacturers, will in all probability result in most important improvements in the system adopted for the purification of iron.

It will be difficult in this report to separate the considerations relating to the reduction of iron from its ores, from those which have reference to the purification of the metal, or the production of particular descriptions of iron; as many of the patents to which

it may be necessary to allude are connected with more than one branch of iron manufacture, such, for example, as those which relate to the application of particular agents, at different stages of the manufacture, or which propose methods for combining the smelting and refining processes.

Any attempt at classification must, therefore, rather have reference to the principles involved in the various patented processes discussed, than to the separate stages in the manufacture of iron.

The most simple modifications proposed of late in connection with the smelting process, relate

1°. To the construction of the blast-furnace ;

2°. To the application of the blast ;

3°. To the mixture of ores, &c., with a view to ensure uniformity in the working of the furnaces ;

4°. To the preparation and state of division of the ore, and its mixture with the fuel and flux ;

5°. To the description of fuel employed in the blast-furnace.

6°. To the economisation of the fuel employed.

Of such modifications, those included under the first four and the sixth classes, which have been made public as patents within the last two or three years, are scarcely of such a nature as to rank as improvements of high importance ; neither can it be supposed that they fairly represent the general progress which has been made in the details of iron smelting. It will, therefore, suffice to mention as examples of these classes of patents :

That Mr. Charles Howard (1854) proposes to cleanse thoroughly and to granulate the ores, to mix them in proper proportion with the fuel and flux in a divided condition, and to convert the mixture into a suitable form for smelting by compression into cakes ;

Sir Francis Knowles (1852) and Mr. C. Cowper (1853) have patented proposals for mixing rich ores with slags from copper-works ; for the use of schist, in admixture with similar ores ; and for the employment of other minerals with ores of different classes, in order to ensure uniformity of product from the blast-furnace ;

Mr. Crane (1854) proposes to employ additional blasts at some distance above those passing from the usual tuyères into the furnace ;

Messrs. Lea and Hunt (1852) and Mr. Prideaux (1853) apply the gases, obtained in the preparation of coke for the blast-

furnace, as a source of heat in the puddling and other processes, and Mr. Mickle (1855) conducts the gases thus collected, after their admixture with the air necessary for their combustion, into the blast-furnace, in which the smelting process has been carried on as usual, with coke. Mr. Onions proposes to collect the waste gases from boiler fires and other sources in iron works for the same purpose.

The proposals which relate to the *description* of fuel to be employed in the smelting process, possess considerable interest, as they include patents for the application of peat in various forms, and proposals for the employment of gaseous fuel for the reduction and treatment of iron.

In Ireland there appear to exist immense deposits of clay-ironstone, which are not worked, or only to a very small extent, on account of the scarcity of mineral fuel, but which have been worked in former times in districts which were then covered with wood. Proposals have been heard of, from time to time, and even very recently, for establishing extensive smelting works in Ireland, in which peat-charcoal was to be employed as the fuel, and I have had occasion to examine some very excellent specimens of pig-iron, in the reduction of which Irish peat-charcoal had been employed.

In Bohemia, iron is profitably smelted with carbonised peat, and from the statements which have been publicly and privately made by Mr. Ommaney, Mr. Dewar, and others, it appears reasonable to expect that a similar result may be obtained in Ireland. Two recent patents may be referred to, in order to point out the modes in which peat may be expected to be made available as fuel for the production of iron.

The one taken out by Mr. R. McCall of Limerick (1855) relates, firstly, to the construction of a modification of the blast furnace with closed top and a lateral exit-pipe for the escape of the gases; and secondly, to the use (for smelting, refining, and puddling) of peat, either in its natural or in a compressed state, or of a mixture of equal parts of peat and small anthracite coal, compressed into cakes. He also proposes to work up the refuse turf or peat, by forming it into pulp and then moulding it.

The other patent to which I refer applies to the manufacture of iron with any description of fuel, vegetable or mineral, and appears particularly adapted to iron districts where the attainable fuel is rich in mineral constituents. The patentee, Dr. Gurlt of Prussia

(1856), proposes to effect the reduction and requisite carbonisation of the ore entirely by the gases evolved from the fuel, which is submitted to destructive distillation in gas generators immediately attached to the furnace.

It is well known that in several of the iron districts in Germany, the refining, puddling, and welding processes are accomplished without allowing the metal to come into contact with the solid fuel; the coal, wood, or peat being, in the first instance, converted into gases in generators, which either form part of the furnaces, or are connected with them by conducting pipes. The so-called gas-furnaces, which have been planned by Thoma, Eck, Bischof, and other experienced metallurgists, differ somewhat in their construction, according to their particular object, or the description of fuel with which they are to be worked; their principle may, however, be exemplified by a few words descriptive of Eck's gas-refinery furnace, which is very simple of construction and has met with most successful application, for some years past, at the Government iron works in Upper Silesia, where I had an opportunity of inspecting one in operation a short time ago.

The general construction of the finery is that of a reverberatory furnace, the fireplace of which is replaced by an oblong chamber, nearly four feet wide and about six feet high, and tapering slightly towards the top, so as to facilitate the descent of the fuel, which is introduced through a lateral opening in the upper part of this retort or gas generator.

The air necessary for the production of the gas from the fuel placed in this chamber is supplied by a feeble blast, and enters the generator from the two openings or tuyères of a long air-chest of iron plate, fixed at the back of the chamber, near the bottom. The space between the air-chest and the sole of the chambers serves as a receptacle for the slag and ash from the fuel. There is an opening below the air-chest, through which fire is introduced into the chamber, when the furnace is set at work, and which is then bricked up, until, at the expiration of about fourteen days, it becomes necessary to let the fire die out, when the slag and ashes which have accumulated on the sole of the generator are removed through this opening. When a brisk fire has been kindled in the generator, and the lower opening closed up, a moderate supply of air is admitted through the tuyère into the chamber, which is filled with coal after a sufficient quantity has become thoroughly ignited. It is evident that the fuel is in this

way made to furnish the maximum quantity of inflammable gas, undergoing destructive distillation as it gradually descends in the generator, and furnishing carbonic oxide as the secondary product of the combustion of the coke or charcoal formed. As the gases rush towards the hearth of the furnace, they meet with a supply of air, passing from a series of tuyères which enter from an air-chest into the top of the furnace, just over the fire-bridge, at an angle of 30° ; the resulting flame being thrown upon the metal on the hearth, in front of the bridge. Both air-chests communicate with an accumulator, and the supply of air to the tuyères admits of perfect regulation by means of stop-cocks. The pressure of air employed is about 4 lbs. to the square inch.

When the charge of iron on the hearth is ascertained to be thoroughly fused, a small quantity of crushed limestone is thrown over its surface, and two tuyères are then introduced into the furnace at an angle of 25° , through an opening on each side of the hearth not far from the bridge; the width of the nozzle employed depends upon the power of the blast used. The air, rushing from these tuyères, impinges with violence upon the iron, and, the two currents meeting, an eddying motion is imparted to the fused metal. In a short time the motion produced in the mass is considerable; the supernatant slag is blown aside by the blast, and the surface of iron thus exposed undergoes refinement, while it changes continually, the temperature of the whole mass being raised to a full white heat by the action of the air. The iron is also stirred occasionally in order to ensure a proper change in the metal exposed to the action of the blast. A shovelful of limestone is occasionally thrown in (the total quantity used being about 1 per cent. of the crude iron employed). The duration of the treatment in this furnace, after the fusion of the metal with a charge of about 40 cwt., varies from two and a half to five hours, according to the product to be obtained.

When the charge is to be withdrawn from the furnace, the side tuyère nearest the tap-hole is removed, so that the blast from the opposite tuyère may force the metal towards the hole. The fluid iron, as it flows from the tap-hole, is fully white hot and perfectly limpid; it chills, however, very rapidly, and soon solidifies.

The loss of metal during the treatment is said not to exceed 5 per cent. The extent to which the iron is purified by treatment in a furnace of this description may be discussed hereafter. The above brief description has been given to demonstrate the sim-

plicity of the arrangements, the great facilities which they present for regulating the temperature and the oxidizing effects of the flame, and the economy in fuel which must attend its employment in such a manner as that described. It must also be remembered that the fluid metal is not allowed to come in contact with the mineral constituents of the fuel.

The arrangements proposed by Dr. Gurlt for the reduction of iron by gaseous fuel are based upon those above described. The roasted ore is reduced to fragments, presenting a certain uniformity of size, and placed in a sloping cylindrical shaft or cupola, the lower portion of which communicates with two such generators as that just described. The gases, as they pass from these into the furnace, are supplied with air just sufficient to kindle them; the ore is raised to a dull red heat, and, at that temperature, undergoes, in the first instance, reduction, and then the requisite carbonisation by cementation. The product gradually sinks into a cooler portion of the furnace below the openings of the generators, and, upon subsequent removal, is subjected to fusion with the necessary flux, in a simple modification of Eck's furnace provided with two gas-generators and blast appliances, at the opposite ends of the hearth. Dr. Gurlt considers that the process of which the above is an outline will furnish products of a high degree of purity, whatever be the description of fuel used, and that the nature of the iron obtained may be regulated by the duration of the process of cementation, in the first furnace, and by the subsequent treatment in the smelting furnace. It is scarcely necessary to enumerate the advantages which he claims for his process, such as the possibility of using any kind of fuel; the complete separation of the mineral constituents of the fuel from the metal; the more perfect carbonising action of gases upon the porous metallic mass obtained; the possibility of arresting this process of cementation at any point, so as to regulate the nature of the product; the economisation of fuel; the ease with which large quantities of steel may be rapidly fused in his smelting furnace, &c. It is to be hoped that these most important advantages, the theoretical correctness of which cannot be disputed, may eventually be fully confirmed by practice.

The possibility of effecting the reduction of iron and its purification, or conversion into the particular description required, by one continuous process, is a problem which has engaged very considerable attention of late; an examination, however, of the patented processes for attaining this object, does not lead to the

conclusion that a process has as yet been elaborated which can compete successfully with the present system. The general nature of the plans suggested may be illustrated by the following examples :—

Mr. Augustus Bellford (1854) proposes the treatment of a mixture of ore, carbon and flux, in tubulated vessels, and subsequent fusion of the reduced metal in crucibles.

Mr. W. E. Newton (1855) places in a cementing oven, alternate layers of coal and ore, with flux if necessary, and maintains the furnace at a white heat for about 48 hours. The layers of ore will then be found to have formed themselves into sheets by agglutination; the metal which these contain is mechanically separated from dross, and fused or welded for employment as spring steel.

Mr. Rogers (March, 1855) and Mr. Congreve (April, 1855), both of New York, have patented contrivances almost exactly alike, for reducing and purifying iron; which consist in placing the mixture of ore and coal in a revolving cylinder, which is so constructed internally, that the mixture is made to travel slowly along from end to end, being exposed during that time to the heat requisite for the reduction of the metal. When the powder arrives at the further extremity of the cylinder, it falls through a hopper on to the hearth of a puddling furnace situated beneath the cylinder.

Mr. J. H. Johnson (1853) effects the deoxidation of the ore on successive tables placed one above another, passing it gradually down to the hotter tables until it arrives upon the lowest, whence it falls into a reverberatory furnace beneath. The ore on the tables is submitted to the action of the gases from this furnace, and is subjected to additional heat from an auxiliary stove or furnace.

Mr. Mackay (1853) has patented the use of a reverberatory furnace with three hearths, and with an arrangement for projecting hot air on to the hearths. The ore and carbon are subjected, in the first instance, to the waste heat from the furnace, and then gradually passed from hearth to hearth, until the reduced and partially refined metal reaches the hearth nearest the fire-place, where it is submitted to the usual puddling process.

The arrangements extensively adopted in various parts of the United States for the manufacture of wrought iron directly from the ore, are far more simple in their nature than any of the proposals above alluded to; it must be borne in mind, however, that

the only ores which are found to be profitably worked, and to furnish products of a proper quality in this manner, are the magnetic and specular ores, and the purer description of hæmatites.

Most of the American furnaces employed for the direct production of wrought iron, are only slight modifications of the Catalan forge; they are worked with a blast of the usual blast-furnace-pressure, and which is frequently heated by the waste heat from the *bloomery-fire* (as these forges are called). The fuel employed is charcoal, and the method is acknowledged to be a wasteful one.

In the various patented projects relating to iron-manufacture, already referred to in this report, the points of novelty are all connected with the method of effecting the reduction and purification of the metal by the usual agents—fuel in the solid or gaseous form, and air—with the addition of such mineral substances as are generally employed as fluxes, when necessary. It could scarcely be imagined that other well known and powerful chemical agents, the efficacy of which, for effecting the purification of iron, is predicted by theory, should escape trial, or even application, in that direction. Among such agents chlorine stands prominent, and the proposals for the employment of that agent, in one form or another, have been correspondingly numerous.

In 1851 Mr. Crace Calvert patented the use of chlorine, chlorides, hydrochloric acid, and hypochlorites, in connexion with iron smelting and the purification of coke. In his patent he proposed to bring chlorine, as a gas or a compound (chloride of sodium being preferred), in contact with the ore when roasted, or with the materials in the blast furnace; the gas being passed into the furnace about ten feet from the top of the charge, before the reduction of the metal takes place, or the compounds of chlorine being thrown into the top of the furnace with the other materials. If a compound were used, he considered that its base would also exert a purifying action, tending to the removal of the sulphur and phosphorus from the metal.

The idea of purifying or preparing the coke to be employed for iron-smelting by chlorine and bases, has been acted upon with a slight modification by Mr. Prideaux (1853), who, in a patent already alluded to, proposes to drench the glowing coke with lime-water, containing either common salt or carbonate of soda, or other similar salts.

In the production of cast steel, M. Fontaine, of Paris (1855),

has proposed to pass chlorine or hydrochloric acid over the surface of the metal, or to treat it with a mixture of a chloride or hypochlorite of an earth or alkali, iron-scale and binoxide of manganese. This treatment is to be carried on, either in pots or in the puddling furnace. Mr. Martien, of New Jersey (1856), has very recently taken out a patent for the employment of various materials for the purification of iron, which are to be passed through the liquid metal; and among these chlorine is specified. Mr. Tilghman, of Philadelphia (1856), follows close in the footsteps of Mr. Calvert, by proposing to introduce powdered chloride of sodium together with the blast, or by other convenient means, into the *lower* part of the furnace.

Various compositions, of which chloride of sodium or chlorides form an essential constituent, have also been patented for employment as fluxes in the manufacture of steel and of malleable iron. Chloride of sodium appears also to be very frequently used on the Continent, in the puddling process, and in the manufacture of cast steel. A statement recently made by Mr. Kenyon Blackwell, in a paper read before the Society of Arts, to the effect that chloride of sodium was much used under those circumstances at the Seraing Works in Belgium, elicited the observation from Mr. David Mushet, that his father had patented the use of chloride of sodium in the puddling process about thirty-three years ago.

Bin oxide of manganese is another agent included in many recent patents connected with the manufacture of iron, and very frequently in association with chlorides. Mr. Brooman (1854) has patented a mixture of two-thirds chloride of sodium and one-third bin oxide of manganese, for purifying and softening steel; and, more recently (1856) another, for the conversion of bar-iron into cast steel, by a single melting, and which contains bin oxide of manganese, chlorides of sodium and ammonium, and ferrocyanide of potassium. Mr. Leachman (1853) adds a mixture of bin oxide of manganese, chloride of sodium, and calcined clay to iron, during the boiling process. In several patented processes for the manufacture of steel, the addition of small quantities of bin oxide of manganese is also recommended. Mr. J. Crowley, of Sheffield (1855), produces malleable cast iron from charcoal pig-iron, by melting it with a very small proportion of scrap-iron, and a mixture of chloride of sodium, bin oxide of manganese, carbonate of lime, and charcoal.

Although the employment of bin oxide of manganese in small

quantities, particularly in the manufacture of steel, has long been a practice frequently resorted to, no very concordant opinions have been pronounced, by authorities on iron, as to the functions actually exercised by that substance. It has been fully demonstrated by analysis, that the quantity of combined carbon in iron, reduced from ores rich in manganese, is always considerable, and that it is so in direct proportion to the amount of manganese which has entered into the constitution of the iron. It is also well known that iron of such a description is particularly adapted for the manufacture of natural steel. The Westphalian and Silesian irons may be quoted as examples. That the facility with which superior steel may be manufactured from manganiferous iron, is *not* occasioned by the retention of a portion of the manganese in the steel as an important constituent, is proved by the circumstance, that the existence of that metal in the steel is demonstrated by analysis to be exceptional; and that steel (such as the Styrian) remarkable for its hardness and elasticity, which has been obtained from ores very rich in manganese, is not found to contain a trace of that metal. The most satisfactory explanation of the beneficial effect of manganese is afforded by the protracted treatment to which it is found necessary to submit iron containing much of that metal, in order to effect its proper decarbonisation, and the facility thus afforded for its more complete purification.

It appears possible that the beneficial effects of binocide of manganese, when added to iron in the manufacture of steel, or in the production of malleable iron, may also be due, in some measure, to the formation of carbide of manganese, and the consequent more obstinate retention of a portion of the carbon in the iron. Other advantages may be ascribed to the greater fusibility of the slag produced, when manganese is employed, and also to a diminution, under these circumstances, of the destructive effect of the slag upon the crucible or hearth, during the operation of smelting and decarbonising. It is also stated that the presence of a small quantity of manganese in the steel has the effect of improving the texture and colour, and of imparting to it the property of welding readily to wrought iron.

While referring to manganese in connexion with iron, it may be mentioned that some attempts appear to have been made within the last few years, to examine into the influence exerted over the properties of iron by the presence of small quantities of other

metals, and to ascertain whether iron may not be advantageously hardened or toughened, or its properties in any other way modified, by being alloyed with small quantities of such metals as zinc, copper, tin, lead, &c.

Several proposals were made public not long since, through various channels, for the employment of copper, nickel and zinc for increasing the tenacity of iron, and thus improving its quality, for such purposes as the manufacture of ordnance.

These proposals appear, however, to have been the result of inference rather than of experiment; the arguments in their favour being sought in such circumstances as the reported superior toughness of iron made from Franklinite; the peculiar character of meteoric iron; the existence of an appreciable amount of copper in the highly tenacious steel from Solingen, &c.

Messrs. Talabot and Stirling appear, however, to have devoted some attention to the subject, and have patented proposals, in which the addition of small quantities of various metallic oxides (*e.g.*, those of tin, zinc, barium, calcium) to the iron is recommended, for the purpose of modifying its properties in different ways. The method generally suggested for their application is to line the sole of the puddling furnace, or the pig-moulds or chills, with sawdust, bitumen, or tarry matter, mixed up with a small quantity of the particular oxide, and with oxide of iron. The uniform alloy is supposed to be formed in the subsequent treatment of the metal. Although it is not on record that these and similar proposals have led to any practical results, there is little doubt that the influence of foreign metals upon iron will receive the serious attention of some of the metallurgists who are just now zealous in the cause of iron-manufacture, and that results of interest and importance may be expected from a farther prosecution of such experiments as those instituted by Faraday and Stodart some years ago, with particular reference to steel.

Attention is naturally directed, by the discussion of the subject of alloys, to the successful results which appear to have attended experiments made with a view of producing steel or other specific varieties of iron by the very simple process of mixing together, in proper proportions, iron-varieties of different composition.

Several patents have been published within these last two years, for the preparation of mixtures of this kind: thus, Mr. Bessemer (1855), in two patents relating to the melting of steel, and its manufacture by cementation, claims the production of a mixture

of cast iron and steel, prepared by adding together the two liquid materials, or by immersing the solid steel in the fused cast iron. The products are susceptible of annealing or hardening like steel. Dr. Price and Mr. Nicholson (1855) have found that a very superior description of metal is produced by mixing grey pig-iron with the so-called finery-metal, which, though it still retains nearly the whole of the carbon originally contained in the iron, is comparatively free from silicium, and has also parted with a certain proportion of its other impurities. The product thus obtained, containing as it does a considerable portion of the carbon in a combined state, bears great resemblance to the description of iron, manufactured for ordnance at all the Continental gun foundries, by careful mixture of pig-iron with partly refined products, and subsequent protracted treatment in the reverberatory furnace.

Messrs. Price and Nicholson (1855) have besides secured a patent for the manufacture of steel of excellent quality, by melting together finery-metal and wrought iron. Mr. G. Brown (1856) also proposes to make steel by a mixture of metals, but employs charcoal-pig-iron, and wrought iron made from the same material. Mr. Manevy (1856) prepares cast steel by fusing together white cast iron and malleable iron, both previously reduced to small fragments, and with the addition of the oxides of iron and of calcium, potassium, or sodium, in some form. There can be no doubt that, provided the necessary precautions be taken to ensure the uniformity of the materials employed, the production of cast steel by the simple mixture of iron-varieties of a known composition should possess considerable advantages over the process of decarbonisation.

Before proceeding further with the examination of the recent improvements in the manufacture of steel, it is advisable to complete the review of the patented proposals, relating to modifications of the ordinary methods of refining and puddling.

Mr. Kenyon Blackwell, in his paper on the manufacture of iron, already referred to, alludes to the difficulty experienced in the treatment of grey iron in the puddling furnace, on account of its fluidity, and the tenacity with which it retains its carbon; and in pointing out the great loss of iron sustained by the intermediate treatment in the coke-finery, which it is necessary to adopt, suggests that the partial decarbonization of the metal might be far more economically effected by its treatment in a small blast-furnace, similar to the cupola used for remelting, with the addition,

perhaps, of minerals consisting of nearly pure oxides of iron. That some such treatment has occasionally been adopted, is shown in a subsequent communication from Mr. D. Mushet, who states that his father patented, in 1817, the use of the cupola for remelting and partially refining iron, and employed the method in Staffordshire and Wales. The adoption of a similar treatment is also referred to, in one or two comparatively recent patents connected with refining.

Mr. D. Mushet moreover claims for his father the first patent for employing hæmatite in the refining or puddling of grey iron, a method of treatment which is also brought forward in several forms in recent patents.

It has been noticed, in connexion with Mr. Calvert's patent, that importance is sometimes attached to the effects of the metals of the alkalies and earths, as agents for the removal of such impurities as sulphur and phosphorus from iron. Various proposals have been patented within the last two years, for the employment of alkalies and similar agents, as fluxes. Mr. Hampton (1855) slakes quick-lime with the solution of an alkali, or alkaline salt, and employs it in the refining and puddling furnaces. MM. Du Motay and Fontaine (1856) purify and decarbonise iron in the refining and puddling furnace, by the employment of fluxes prepared from the scoriæ of the puddling furnace, from oxides of iron and silicates or carbonates of alkalies, or other bases. Mr. Pope (1856) proposes to add the residue obtained by the distillation of Boghead or Torbane mineral, to such fuel as is employed in the refining of iron, and also includes the use of spent oxide of manganese in his patent. Mr. Sanderson, of Sheffield (1855), employs, for the refining of iron, such substances as sulphate of iron, capable of disengaging oxygen or other elements which will act upon the silicium, aluminium, &c., contained in the metal.

The specification of the objects of the latter patent leads me to the consideration of a patent granted to Mr. J. Nasmyth in 1854, for an improvement in the puddling process, which is particularly worthy of notice, as being the first application of the principle upon which several interesting patents connected with iron-refining are based, to which I shall shortly refer. The patent claims the treatment of iron with a current of steam, which, being introduced into the lower part of the iron in the puddling furnace, passes upwards, and, meeting with the highly heated metal, undergoes decomposition, both elements acting as purifying

agents. The steam employed is at a pressure of about five pounds per square inch, and passes into the metal through a species of hollow rabble, the workman moving this about in the fused metal, until the mass begins to thicken, which occurs in from five to eight minutes after the introduction of the steam; the steam-pipe is then removed, and the puddling finished as usual. The advantages claimed consist in the time saved in each heat or puddling operation (from ten to fifteen minutes); the very effective purification of the metal, and the possibility of treating highly carbonised pig-iron at once in the puddling furnace, the preliminary refining being thus avoided. It is said that this method of treatment, after having been used with great advantage for two years at the Bolton Iron Works, is gradually extending itself to other large manufactories.

Another, though less striking, application of water in refining iron is made by Mr. W. Taylor (1855), who, after puddling the metal until it is pasty, runs it into water; the spongy mass thus produced is ground by rollers, separated into powders of different degrees of fineness by sifting, and melted. The portion of metal oxidised by this treatment is to serve as the final purifying agent. The quality of the product varies with the fineness of the powder. Mr. Martien, of New Jersey (1855), proposes to use a very similar mode of treatment for the conversion of ore, reduced to spongy metal, into steel. The water into which he throws the heated mass contains, in solution, saline matters, such as chloride of sodium, borax, soda, &c.

The principle of employing oxides of iron as agents for decarbonising the metal sufficiently to produce steel, has recently occupied the attention of several metallurgists. One or two patents involving its application have already been published; other modifications are in course of elaboration; and it is considered likely, by competent authorities, to receive, in some form or other, extensive application.

In 1854 Mr. Stirling proposed to produce cast steel by adding to fused cast iron a quantity of the oxides or carbonates of iron, the operation being performed in crucibles or reverberatory furnaces, and being repeated with successive quantities of the ore, until the proper description of steel had been produced. From five to seven per cent. of the oxides were to be employed in the first melting, and smaller quantities in successive operations; manganiferous ores were to be selected in preference to others, and

exceedingly small quantities of other oxides might be added, together with the ore, such as those of zinc or tin, for strengthening, toughening, or hardening the metal.

It will be observed at once, that this process differs only in its details from that more recently patented by Captain Uchatius, of the Austrian Service (1855), which attracted considerable attention last autumn, when a successful experiment was made with it at the works of Messrs. Rennie. The important point in the process of Captain Uchatius, is the great acceleration of the decarbonising effect of oxide of iron upon the pig-metal, by exposing as large a surface as possible to contact with the ore employed. The metal is thus converted into steel in one operation, and with considerable rapidity. The mode of proceeding is to granulate the iron by running the fused metal into water, and beating it with a broom. The globular particles thus obtained are mixed with about 20 per cent. of roasted spathose ore, and 4 per cent. of fire clay, and subjected to the heat of a steel-furnace. The employment of oxide of manganese is not specified; a certain proportion is, however, generally added. The granules of iron are partially decarbonised and melted, and a portion of iron from the ore is also reduced; the increase of yield upon the metal employed amounting generally to about 6 per cent. The granules are sorted in the first instance, as the finer particles produce a softer steel. The addition of a small quantity of wrought iron, in fragments, is recommended for the production of soft welding cast steel, and harder products are obtained by adding various proportions of charcoal to the mixture. The average time necessary for the conversion of such a quantity of iron as was operated upon at the works of Messrs. Rennie (24 lbs.), is said to be about two hours. It is specified that the best description of pig-iron should be employed, and the experiments appear to have always been made with East India pig-iron; but it is believed by the patentee that numerous descriptions of ordinary English pig-metal may be converted without difficulty. The results obtained by Captain Uchatius appear to have been even surpassed by a modification of his process, in which partially refined iron is employed.

Improvements in the conversion of wrought iron into steel by fusion or cementation, have also been made the subject of several recent patents. In one or two processes (*e.g.* for the manufacture of cast steel by Mr. Brooman, and for the production of steel direct from the ore by Mr. Newton,) cyanogen is proposed as an

agent for carbonising; it is either employed in the form of a cyanogen-compound (ferrocyanide of potassium) in a flux, or its production during the cementation process is effected, by the presence of an alkali and animal matter in the cementing oven. M. Bouillet of St. Denis (1854) proposes to use a cementing compound, consisting of glucose or other saccharine matter; horn shavings, dried blood, or other descriptions of animal matter, and wood-charcoal.

As an improvement on the ordinary cementation-process, Mr. Lucas of Sheffield (1854) has patented a method for the conversion of bar-iron into steel in the presence of iron ore, which shall at the same time become converted into steel. The ore is mixed with animal- or vegetable-charcoal, and a small quantity of binocide of manganese; alternate layers of this mixture, iron fragments and charcoal are piled in the converting furnace. When the conversion of the iron into steel is effected, the reduced ore is melted, and furnishes cast steel.

In 1855, Mr. Bessemer obtained three patents for the manufacture of steel. The first two, which have already been alluded to, as including the preparation and treatment of mixtures of steel and cast iron, relate to particular arrangements for carrying on continuously the cementation process, by allowing the cut bar, granulated puddle-iron, or other refined metal, and charcoal, either to travel gradually along a horizontal heated cylinder (which is divided into chambers by plates linked together, and moved slowly along by a winding apparatus); or to descend gradually in a vertical cylinder or retort, which is charged with material from above. Various improvements in the arrangement and construction of the furnaces and crucibles are included in these patents.

The third patent, dated October, 1855, relates to the treatment of iron, for its conversion into steel, upon the principle applied by Mr. Nasmyth to the puddling process in May 1854. The system proposed is as follows:—The liquid iron to be converted is taken from a common finery or cupola-furnace, and filled into skittle-pots, provided with tap-holes at the bottom, and arranged in a suitable furnace. A pipe passes through a hole in the cover nearly to the bottom of the crucible, and is connected with a larger pipe over the furnace, into which highly heated air alone, or air and steam, or steam alone also highly heated, is forced, under a pressure exceeding that of a column of metal equal to

the depth of fluid iron in the pots. Thus the air or steam is made to pass up through the liquid metal, and to effect its purification. When the latter becomes pasty or has been treated to the requisite extent, its temperature is raised so as to render it sufficiently fluid for casting. It is observed in the specification that the iron is liable to become pasty by treatment with steam, which may be avoided by properly maintaining the heat in the pot-furnace; but that it is found advisable to use steam only at an early stage of the process, and to conclude the treatment with air, which readily maintains the iron in a liquid condition, and also rapidly raises its temperature when it has become much lowered by the treatment with steam.

In the specification of this patent, Mr. Bessemer intimates his knowledge of Mr. Nasmyth's process for puddling with steam, and of a patent taken out by Mr. Martien of New Jersey, earlier in 1855, for effecting the partial purification of iron, by causing air or steam to pass up through the liquid metal, as it flows along gutters from the tap-hole of the blast-furnace or finery-forge, but especially from the former. By this treatment, no more than the partial purification of the metal is attempted, and Mr. Bessemer, therefore, lays claim in the above patent to the conversion of crude iron into malleable metal or steel, by the treatment with air and steam, in the manner described.

This patent of Mr. Bessemer's is followed by two others (in December 1855 and July 1856), in which the treatment of iron by air and steam is carried out in various ways, and which are, in a manner, preparatory to the patent for the refining of iron without fuel, on the subject of which a paper was read by Mr. Bessemer at the British Association last year, and which, for some time, excited the general attention of the iron-manufacturers and the public.

In the first of these patents it is proposed to refine the iron by passing air or steam into the liquid metal, which has been transferred from the blast-furnace to a species of ladle, on trunions, and then to submit the product to further treatment with air, on the hearth of the puddling furnace, or in long retorts. Or, the metal is treated with steam or air in a large crucible, enclosed in a circular reverberatory furnace. A clay pipe serves to conduct the steam or air to the bottom of the crucible. It is again observed that steam should only be used at the commencement of the operation, and that, if the metal becomes pasty, the heat of

the furnace should be raised prior to tapping. The patent includes a proposal for recarbonising iron in this crucible, by raising the heat of the metal, in the first instance, by the injection of air or steam, and by then forcing carbonaceous gases, or solid carbonaceous matter into the iron, through the same channel.

The second patent is for the exposure of liquid iron, in a finely divided condition, to the action of a current of air. One method proposed for effecting this, is to have two cupolas, so arranged, that they may be alternately lifted and depressed. Both being charged with highly heated fuel, and the one containing a quantity of fluid metal; they are so arranged that the latter may be run from the tap-hole into the top of the second cupola. As the iron descends in a shower through the fuel in this cupola, it meets with a powerful current of air passing upwards. When the whole of the iron has been run out from the upper cupola, the relative position of the two furnaces is changed, and the metal is poured back upon the fuel in the first cupola, which is now lowest, and through which a blast is also passing. This operation is repeated until the metal has been sufficiently refined. Or, the iron is fused in a furnace which may be provided with internal projections, and which is made to revolve on horizontal axes so that the metal, when fluid, may be raised by the projections, or by centrifugal force, and allowed to fall upon the heated fuel, through which air circulates. The axes are hollow, a blast being admitted through the lower, while the upper one provides for the escape of the products of combustion. It is stated that coke may be used as the fuel, and that, if the object is to obtain steel, an addition of from 1 to 2 per cent. of binocide of manganese and a similar proportion of chloride of sodium should be made to the metal.

Immediately upon the above patents, followed the proposal of Mr. Bessemer to produce steel and malleable iron from the crude metal, without the use of fuel, to the details of which it is scarcely necessary to allude, as the process in question has not only been very fully discussed in public, but also witnessed by a great number of persons interested in iron manufacture. It will be sufficient to bear in mind that a suitable vessel, provided near the bottom with several tuyères, in connection with a blast-cylinder capable of compressing air to about eight or ten pounds to the square inch, is placed in the immediate vicinity of a cupola or blast-furnace, so that the liquid metal may at once run into it. The vessel, which is closed at the top, is provided with lateral

openings, to be used for the introduction of the metal, and the removal of the product. The blast having been turned on into the furnace or converting vessel, the fluid metal is allowed to run in. The iron is at once violently agitated, and a considerable number of sparks issue from the furnace, accompanied by a small carbonic oxide-flame. When this operation has been carried on for about fifteen minutes, the temperature of the metal gradually increasing, the action of the air appears to become more intense; the metal rises considerably above its actual level; the heat is raised to full whiteness, and a frothy slag is thrown off from the surface in considerable quantities. In a few minutes the size of the flame issuing from the furnace, increases considerably, and it is steadily maintained for about ten minutes, when it rapidly diminishes, and the process is then considered complete. Upon tapping the furnace, the metal runs freely and is perfectly white hot, but it chills very rapidly, and, from the number of cavities generally observed in the masses cast, it appears to solidify before the air-bubbles, carried into the metal as it pours into the mould, have time to rise to the surface. Mr. Bessemer claims the production, by this operation, of pure, homogeneous, malleable iron, and also the preparation of hard or soft steel, and of a particular product called semi-steel, by arresting the operation at certain periods, indicated successively by the phenomena above alluded to.

In discussing the theory of these processes in his paper, read to the British Association, Mr. Bessemer considers that, during the first part of the treatment, the oxygen of the air combines with the graphite in the iron, producing carbonic acid, thus raising the temperature considerably. Subsequently, when the metal has become very highly heated, and the flame is observed to increase; the combined carbon undergoes oxidation. At this stage of the process, as the quantity of carbon present is but small, a portion of the iron is stated to undergo oxidation, being immediately fused, and disseminated through the metal, upon which it acts as a powerful solvent of the silica and earthy bases. The sulphur and other volatile matters are also supposed to be oxidised and removed at this period. The iron is stated to undergo complete purification by this treatment, while the loss of metal during the operation is considered to be about 10 per cent. below that usually sustained in its purification.

Before examining into the extent to which the views of Mr.

Bessemer have been borne out by practice, it is necessary to state that the patent last alluded to, was followed, shortly afterwards, by another, providing for the adaptation of the process just described to the furnaces used for smelting, re-melting, and refining iron. Another form of converting vessel was also proposed, for ensuring the contact of the air with a larger surface of metal, previous to its escape. In order to obviate the injurious effect, upon the malleability of the product, which the presence of any oxide of iron would exert, it was proposed to treat the refined metal with some form of carbonaceous matter, or to add the latter towards the completion of the refining process. Treatment with carburetted hydrogen, or carbonic oxide; the introduction of a pole into the liquid metal; or the addition of charcoal, anthracite, or carbonate of iron, are the methods specified.

It has already been stated that Mr. Bessemer does not stand alone in proposing the purification of iron by treatment with steam or air. The patent of Mr. Martien for passing air and steam through fluid iron, has already been noticed. A subsequent patent, by the same gentleman, includes the application of other purifying agents, together with the air and steam; such as chlorine, hydrogen, and coal-gas. Oxides of manganese and zinc are proposed by him to be blown into the iron, to assist in the removal of the silicium; spathose ore is to be similarly applied, to assist in decarbonising the iron; and a small quantity of clay, to facilitate the working of the metal.

Mr. John Birch, of Bradford patented, in June 1855, proposals for refining crude iron, immediately upon its removal from the blast-furnace in a molten state, by allowing it to flow into an improved refinery-furnace adjoining; and for smelting and refining iron in one operation, by the employment of, what he terms, reducing and oxidising tuyères, in connection with a peculiarly constructed blast-furnace, so arranged that the metal, as it is reduced, collects in a deep hearth and is there at once submitted to the refining action of the air from the oxidising tuyère. The employment of steam in admixture with cold blast in the smelting furnace and finery-forge, was made the subject of a patent by Messrs. Armitage and Lee, of Leeds, in October, 1856, and in August a patent was taken out by Mr. G. Parry, furnace manager at the Ebbw Vale works, for the purification of iron, by means of highly heated steam. The fluid iron is allowed to run into a reverberatory furnace, previously heated, and the steam is

either made to impinge upon it from several tuyères, or to pass through the metal. Steel is to be obtained by treating highly carburetted iron with the steam, and then either running it into water and fusing it, with the addition of purifying agents, or adding to it, in the furnace, a small quantity of clay and, afterwards, about 10 or 15 per cent. of calcined spathose ore.

It would be quite out of place, in this report, to enter into any discussion with reference to the respective claims to originality of the different patentees who propose the partial or complete purification of iron, and the production of steel, by the passage of air and steam through the metal; but it will be generally admitted that to Mr. Bessemer the credit is due of first directing the attention of iron manufacturers and the scientific world, prominently, to this mode of treatment, and of awaking a spirit of more scrutinizing inquiry, than had before existed, into the extent to which iron is purified by being subjected to the action of air or steam. The announcement, so convincingly demonstrated by experiment on a large scale, that the heat evolved by the action of air upon iron when once liquid, was sufficiently intense not only to maintain the fluidity, of the metal, but to raise it to a heat attained only in the most powerful furnaces,—so that the purifying action of oxygen, in the gaseous state, was promoted to the fullest extent,—was received with general astonishment, and, by the chemist, with wonder, that a fact so self-evident should furnish such important results as those described by Mr. Bessemer in his paper, and yet so long have escaped application.

The simplicity of the process, the positive statements made by Mr. Bessemer in support of his arguments for proving that the purification of the metal must be complete, and his very attractive assertions with respect to the economy of his process; all combined to raise to the highest the general expectations of the important results to be attained by its adoption in iron-manufacture.

It need scarcely be stated that these expectations have not yet been realised, and that the ultimate product, which Mr. Bessemer obtains by the process just now described, has been found to differ in some very material respects from the malleable iron obtained by the old puddling process. Both the economy and efficacy of Mr. Bessemer's method for purifying iron have been contested by the publication of facts resulting from experiments with the process and the product, and from chemical investigation.

I will not attempt to enter into any discussion of the technical objections raised against the adoption of such a process as that of Mr. Bessemer's, as a good method for obtaining malleable iron, but will confine myself to a few remarks, bearing upon the chemical questions involved in the proposed system of refining, some of which I venture to offer with considerable hesitation, as the results of limited observation and experiment.

It has been amply demonstrated that the constituent of cast iron, which may be regarded as generally exercising the greatest influence over its quality, namely, the silicium, is also that which may be most readily and completely abstracted from the metal, by its subjection to oxidising influence. Those specimens of iron refined by Mr. Bessemer's process, which have been chemically examined, were found perfectly free from silicium. Iron which has been subjected to a less searching treatment with oxygen in the Silesian gas-finery furnace of Eck, has been found to be almost perfectly freed from silicium, and the pig-iron generally operated upon in these furnaces contains from 4.5 to 5 per cent. of that constituent. The patents of Messrs. Price and Nicholson which have been referred to, are based upon the observation that the product of the ordinary finery, obtained from iron of moderate quality, contains only a very small portion of silicium.

The statements of these gentlemen, that the actual amount of carbon existing in finery-metal, differs little from that originally contained in the pig-iron, substantiates similar observations made by me with reference to products of the refining process.

It may, therefore, be considered as very probable, that no appreciable amount of carbon is oxidised, upon treatment of pig-iron by such a process as that of Mr. Bessemer, until, as a first effect of the high temperature, the graphite has become converted into a carbide of iron; and that, during the interval which elapses before the carbide undergoes decomposition, the silicium is almost or entirely oxidised.

It will be generally admitted that among the elements in the pig-iron, with which the oxygen meets at a high temperature, the iron itself will be one of the first to undergo oxidation, and that the increase of temperature, resulting from the contact of air with the fluid metal is, in the first instance, almost entirely due to this oxidation of iron, which will be partially checked for a time, when the temperature is sufficiently high to favour the oxidation of the combined carbon.

The compounds formed by sulphur and phosphorus in iron appear to be far less easy of decomposition than would have been imagined *à priori*. From an examination of the finery metal from the English or Silesian furnace it appears that at the period when the carbon begins to undergo oxidation, the sulphur and phosphorus remain almost untouched; the analyses of several specimens of Mr. Bessemer's ultimate product have shown, moreover, that these elements, as they exist in the metal, have not undergone oxidation to any important extent, even when the carbon has been almost entirely removed; although the action of the air is assisted, as Mr. Bessemer describes, by the oxide of iron, produced during the treatment, which becomes to a certain extent mixed up with the agitated metal.*

The important obstacle to the successful purification of iron, by subjection to treatment with air, even in the most complete manner, evidently consists in the difficulty of effecting the decomposition of the compounds of sulphur and phosphorus to a sufficient extent; or perhaps still more, in the impossibility of removing their oxides, when produced, from the reducing influence of the highly-heated metal.

There is some reason to believe that the effect of nascent hydrogen from steam, upon the sulphur and phosphorus in iron, is more energetic than that of oxygen from air; but the use of steam appears, as might have been expected, to have the effect of cooling the metal rapidly to such an extent as to diminish its fluidity; hence Mr. Bessemer's reason for only recommending its application at the outset of the process. It is stated, however, that Mr. Parry has, by the use of highly-heated steam, recently obtained very successful results.

The phenomena observed on the treatment of iron by Mr. Bessemer's plan, added to the inferences drawn from the facts above alluded to, would appear to lead to the following explanation of the effects successively produced by the passage of air through the liquid metal:

In the first instance, a portion of the iron undergoes oxidation,

* I am unware whether Mr. Bessemer ever caused the amounts of sulphur and phosphorus to be determined in metal, before and after treatment; the specimens of his products which I have examined contained from 0.4 to 0.5 per cent. of phosphorus, and from 0.05 to 0.06 per cent. of sulphur. These specimens were stated to have been prepared from Blœnavon iron, in which the percentage of phosphorus has been found to be about 0.5, and the sulphur 0.06. I have been informed that similar results have been obtained by other chemists.

the temperature of the mass being thereby very considerably raised. At the same time the conversion of the graphite into carbide of iron gradually takes place, while the silicium undergoes oxidation and contributes to the formation of slag. When the scintillations are observed to diminish in quantity, while a steady flame makes its appearance and the action becomes more tumultuous, the decomposition of the carbide of iron commences; the oxidation of the iron still continuing, however, during the production of the carbonic oxide. When the flame ceases to appear, the purifying functions of the air seem to have attained their limits; but the sulphur and phosphorus still remain in the metal, in but slightly diminished quantities. If, therefore, the original proportion of these elements in the iron operated upon are inconsiderable, the product may exhibit most of the attributes of the best malleable iron; but if the percentage of sulphur or phosphorus in the crude metal be at all considerable, the influence exerted by these substances over the properties of iron must be exhibited in the product, even in an exaggerated degree.

Without entering into the question of economy, with reference to such a mode of treatment as that proposed by Mr. Bessemer, it is evident that, unless means are ultimately devised in connection with it, for promoting the removal, to a considerable extent at any rate, of the sulphur and phosphorus from the iron, it cannot compete, as regards the quality of the product, with the old puddling process; in which the decomposition of the sulphur and phosphorus compounds in the iron, and the removal of these elements from the metal, is mainly effected by prolonged contact of the latter with the oxidising slag.

The tedious and laborious nature of the puddling process, and the circumstance that the skill and industry of the operator determine, in great measure, the quality of the product, are alone reasons sufficiently powerful to induce all interested in the manufacture of iron to cherish the hope, that the unceasing attention and study which Mr. Bessemer and many other metallurgists are at the present time devoting to the subject of iron refining, may result in the elaboration of a process really capable of fulfilling the high expectations entertained, in the first instance, of the system of treatment which, associated with the name of Mr. Bessemer, enjoyed for a brief period so large a share of popularity; but which must undergo some vital modifications ere it can offer a prospect of realising the prophecy of Mr. Nasmyth, that a new

era would be established by it in a most important branch of our manufactures.

In the course of the discussion which followed the reading of Mr. Abel's paper,

Mr. P. J. Worsley said that Dr. Gurlt's patent contemplated rather making steel and the higher classes of iron than competing with our present manufacture of cheap iron, although it would seem from all calculations that this process would be very economical, both of fuel and of labour, to say nothing of the power it gives of using any fuel whatever with little risk to the iron.

The division of Dr. Gurlt's patent into two processes corresponding to the upper and lower parts of the high furnaces gives the power of performing each completely without unnecessary heat; a very great advantage, as too high a heat injures the quality; the tendency of hot blast being to give a coarse-grained iron full of large crystals of graphite, from the quarter carburet being decomposed by an excessive temperature into the one-eighth carburet and carbon, beside favouring the absorption of silicium.

The furnace in which Dr. Gurlt proposes to melt the carbonised ore differs from common reverberatory furnaces in having means to control the atmosphere of the furnace by regulating the supply of wind, so that this furnace is, in fact, a gigantic blow-pipe with its oxidising and reducing flames, and with what will be still more useful, its neutral flame. With this, Dr. Gurlt hopes to melt steel in quantity without altering its quality, and thus be able to cast large pieces of the same metal, an object never hitherto attained.

Mr. John Taylor observed—

The process proposed by Mr. Bessemer for the conversion of cast into wrought iron having been noticed by the Society, in connection with the subject of the paper now read, and I having witnessed that process at the Dowlais Iron Works, may, perhaps, be permitted to observe that the general result obtained at those works was, that it was quite impossible to make malleable iron from the same description of pig iron that is usually employed for the manufacture of rails.

It is doubtless well known to the great majority of the members present that iron, as it runs from the furnace, may be roughly divided into two kinds—one in which nearly if not the whole of

the carbon is in chemical combination with the iron, forming a white brittle iron, and which, by proper treatment, is readily converted into malleable iron. This species is known by the name of white forge pig. The other species of iron is termed grey foundry pig; in it the carbon exists not only chemically combined with the iron, but also diffused mechanically through the mass in a more or less crystalline state: this species is almost wholly employed by the founder. It is, however, to be observed that between these two varieties, which I take as the two extremes of the scale, there are numerous sub-species, varying in their relative proportions of combined and uncombined carbon, their purity, their crystalline texture, and other particulars, all of which possess peculiar commercial values, and are known to the trade under certain technical designations.

It was found at the Dowlais works that when grey foundry iron was submitted to Mr. Bessemer's process, in a cupel made after his plan, and air blown into it at a pressure of about 7 lbs. on the square inch, a pig of malleable iron was obtained which possessed all the characters that have been assigned by Mr. Bessemer to the iron manufactured by his plan; but when white forge pig, the same iron from which rails were then being made, was the subject of experiment, the pig, on being transferred to the rollers, broke into several pieces; nor could any of these, by any treatment whatever, even when gently and carefully hammered on the anvil, be brought into the malleable state. In fact, as expressed by one of the overseers, it crumbled like sand. The experiments were conducted by Mr. Riley, the chemist to the works, and on one or more occasions in the presence of Mr. Bessemer. In an economical point of view, it cannot therefore be said that the process has succeeded, at least at present, as the greater price of grey foundry iron over white forge pig would preclude malleable iron made from the former, even by the more rapid process of Mr. Bessemer, from competing in the market with iron made in the ordinary way from white forge pig.

In reference to the phosphorus and sulphur contained in iron, I believe I am not violating any confidence if I say, that Mr. Riley informed me, from analyses made by him, that these substances are not removed from the iron made by Mr. Bessemer.

There can be also, I think, no doubt that the great source of heat in the Bessemer cupel is due to the combustion of the iron itself. The colour and appearance of the flame, together with the

large proportion of scoria and its richness in oxide of iron, together with the relatively smaller amount of iron, confirms this view.

I have the honor of laying before the Society some specimens illustrative of the different stages of iron-making as proposed by Mr. Bessemer, a process which has at least the merit of ingenuity and may at some future time lead to greater results.

XV.—*On the Juice of Beef.*

By CHARLES L. BLOXAM,

PROFESSOR OF PRACTICAL CHEMISTRY AT KING'S COLLEGE.

THE following paper contains an account of an examination of the juice of beef, originally undertaken with the intention of preparing a specimen of flesh lactic acid.

1. 30 lbs. of round of beef purchased in the market, and of excellent quality, were freed from external fat, chopped very fine in a sausage-machine, and stirred up with 3 gallons of cold distilled water; after standing for an hour or two, the mixture was strained, and the meat well squeezed in linen bags.

The mass was then again stirred up with 2 gallons of cold water, and after being squeezed, the operation was repeated a third time with 3 gallons, the last portions of liquid being finally squeezed out of the fibre by a powerful press.

2. The 8 gallons of infusion of beef were then placed in jugs, which were heated in a water-bath till a small portion, having been filtered, was found to remain clear when boiled. The coagulated albumen was separated by a linen strainer, and the clear solution was mixed, in tall jars, with baryta-water, till it had an alkaline reaction to turmeric paper; the precipitated phosphate of baryta was allowed to subside, the clear liquid drawn off, as far as possible, with a syphon, and filtered.

The filtered solution was evaporated to about 2 quarts on a water-bath, and again filtered through a hot-water funnel (for, through an ordinary filter the filtration was extremely slow). It was then further evaporated, on the water-bath, to a syrup, which was kept for some hours at 90°F., and then set aside for four days. It had then become a semisolid mass of crystals of kreatine, which were purified in the usual manner. In this way, 127 grs. of pure kreatine were obtained, and by boiling the amorphous powder

obtained in the purification of the above crystals with their mother liquor and a little animal charcoal, upwards of 70 grs. more kreatine were extracted, giving a total amount of 197 grs. from 30 lbs. of beef. Liebig's estimate of 0.697 gr. from 1000 of ox-flesh, would give 160.5 grs. from 30 lbs.

3. The syrupy mother-liquor originally poured off from the crystals, was set aside for some days, but since only one or two more crystals were deposited, it was mixed with alcohol till it became permanently milky (which required four or five times its volume of alcohol) and set aside.

After some days, a scanty crop of crystals had been deposited. These were carefully examined for Scherer's inosite, but no evidence of the presence of that body could be obtained. The deposit was heated with water, the solution filtered from the considerable undissolved residuc, and gradually evaporated, when it left a syrupy mass, containing a few crystals of kreatine. The liquid washed from these crystals was mixed with chloride of barium, when a scanty precipitate was obtained, which did not present any of the characters of inosate of baryta as described by Liebig.

4. The alcoholic liquid from which these crystals had separated was allowed to stand for some weeks, but, having then deposited very little more, it was mixed with an equal volume of alcohol of 90 per cent., and again set aside.

After two or three days, a portion of the supernatant liquid was tested with alcohol, and, being found to give a very slight milkiness, it was poured off and distilled.

The partly viscid, partly crystalline deposit formed in the strongly alcoholic liquid, was dissolved in water, and a part of the solution was precipitated by chloride of barium; the precipitate did not appear crystalline under the microscope, was scarcely soluble, even in hot water, and did not at all resemble the inosate of baryta. On allowing the aqueous solution of the deposit to evaporate spontaneously, no traces of crystals were perceived—a dark brown resinous mass was left, not affected by ether, but very readily soluble in water.

5. The brown syrupy liquid left in the retort, after distilling off the alcohol, was set aside for ten or twelve weeks, when it was found to have deposited a few crystals.

6. The liquid decanted from these crystals was mixed with 1000

grain measures of dilute sulphuric acid (1 lb. concentrated acid to 4 lbs. water), which produced a copious crystalline precipitate. Enough water was added to dissolve this, and the liquid was distilled, fresh portions of water being continually added, until the distillate was very feebly acid, when 200 gr. measures of dilute sulphuric acid were again added, and the distillation continued; no more acid, however, passing over, the liquid remaining in the retort was violently shaken with 8 fluid ounces of ether. After repeated agitation for several days, the ethereal layer was decanted and distilled; but very little acid being thus obtained, 1 fluid ounce of dilute sulphuric acid was added to the original liquid, which was then repeatedly agitated with fresh portions of ether.

When the amount of acid extracted by the ether appeared to be quite insignificant, the aqueous liquid was mixed with alcohol, till it became decidedly milky (which required more than an equal volume of alcohol), when it was set aside.

7. After the lapse of a week, very little deposit having been formed, more alcohol was added from time to time, until its quantity amounted to about five times that of the liquid. On standing, a considerable crystalline deposit was formed.

8. The solution decanted from this deposit was distilled, to separate the alcohol, diluted with water, and heated with excess of carbonate of lime; the solution, filtered and evaporated, left an amber-yellow syrupy liquid, which did not crystallize on standing, but became opaque when briskly stirred, minute prismatic crystals being then discernible under the microscope; it was dissolved in water, and carefully decomposed with oxalic acid, so as to leave a little lime unprecipitated. The filtrate from the oxalate of lime was evaporated to a syrupy consistence, and since it exhibited no tendency to crystallize, it was reconverted into a lime-salt, by saturation with carbonate of lime, in the hope of obtaining some well defined crystals by very careful evaporation; but only the same viscid mass was obtained, becoming confusedly crystalline when briskly stirred.

The lime-salt was then dissolved in water, and mixed with a strong solution of sulphate of zinc; no sulphate of lime separated at first, but, on boiling, it was deposited as a crystalline powder. The filtered solution, when evaporated, deposited yellow crystalline crusts, very similar to those formed by the lactate of zinc prepared from sugar-lactic acid, but, contrary to Engelhardt's statement

with respect to the lactate of zinc from flesh, these crystals were insoluble in alcohol.

The crystals were freed from adhering mother-liquor, and dried in vacuo over sulphuric acid.

22.17 grs. of the salt, when heated in the water-oven, lost 0.24 gr., and, in the air-bath at 280° , lost, in addition, 0.48 gr. As this loss was so small, and as the brown colouring matter adhering to the salt appeared to have been changed by the heat, I was led to believe that the salt contained no water of crystallisation.

The 21.45 grs. of zinc-salt dried at 280° , dissolved with considerable difficulty in boiling water; the solution was decomposed by sulphuretted hydrogen.

The sulphide of zinc, when converted into the oxide, weighed 4.71 grs., giving 21.96 per cent. of zinc in the salt dried at 280° .

8. The filtrate from the sulphide of zinc, when evaporated on the water-bath, left a yellow, crystalline, very acid residue, containing nitrogen, and burning entirely away when heated. It was very readily soluble in cold water, and the solution was not precipitated by alcohol or by acetate of copper, indicating the absence of inosic acid. The acid was dissolved by hot alcohol, and was deposited, on cooling, in oblique rhombic prisms of considerable size.

The alcoholic solution, when mixed with ether, deposited a crystalline powder, appearing under the microscope to consist of beautiful tabular crystals.

The aqueous solution, when neutralised with ammonia and evaporated, deposited rectangular plates.

After drying in vacuo, the crystals suffered no further loss in the water-oven.

This same acid was found in the ethereal solution obtained at an earlier stage, and supposed to contain the whole of the lactic acid procurable from the beef employed. After distilling the ether from this solution, the brown, somewhat syrupy, acid liquid remaining in the retort was saturated with oxide of zinc, boiled with animal charcoal, filtered, and evaporated. The zinc-salt was deposited very slowly, even from the syrupy solution. On evaporating in vacuo, a viscid mass was obtained, containing a few crystals; this was treated with water; and the crystals washed and dried in vacuo.

Heated in the air-bath to 215° , the crystals suffered no appreciable diminution in weight.

12.49 grs. of the salt were dissolved, though with some difficulty, in boiling water, and the solution was decomposed with sulphuretted hydrogen.

The precipitate, when converted into oxide of zinc, gave 2.80 grs. = 22.42 per cent.

| | | | |
|-----------------|-------|-----------|-----|
| First zinc-salt | 21.96 | per cent. | ZnO |
| Second „ | 22.42 | „ | „ |
| Mean | 22.19 | „ | „ |

Assuming the salt to contain an equivalent of the acid for each equivalent of ZnO, and taking Zn = 32.52, this would give 142 for the equivalent of the anhydrous acid.

(That of anhydrous inosic acid, $C_{10}H_6N_2O_{10}$ (Liebig), would be 174).

The filtrate from the sulphide of zinc, when evaporated, left a residue which possessed all the properties of the acid obtained from the first zinc-salt.

The mother-liquor from the crystals of the second zinc-salt, which would contain any lactate of zinc, was evaporated in vacuo; it left a transparent viscid mass which became opaque when briskly stirred, and was insoluble in boiling alcohol. This mass was dissolved in water, and decomposed by sulphuretted hydrogen; the filtrate, when evaporated, left a brown, viscid, acid residue which was miscible with alcohol, but not to any great extent with ether.

This residue was dissolved in water, and neutralised with baryta-water.

The solution of the baryta-salt, slowly evaporated, left a gummy mass exhibiting no signs of crystallisation. It was decomposed with sulphate of magnesia. (The sulphate of baryta thus precipitated was found to weigh only 17 grs., showing the quantity of acid present to be exceedingly small.) The solution of the magnesia salt, when evaporated to a small bulk, deposited what appeared to be a gelatinous mass, which, when pressed in blotting paper, to free it from adhering mother-liquor, became indistinctly crystalline. This salt, when heated with alcohol, did not dissolve, but broke up into distinct prismatic crystals.

When heated with hydrate of potassa, the salt evolved abundance of ammonia.

I had not succeeded, therefore, in obtaining any lactic acid from the 30 lbs. of beef. It would not be just to assume that the viscid acid liquid last spoken of contained an acid different from the

crystalline acid previously described, since it was evidently associated with much so-called extractive matter, which would account for its not crystallising.

8. The last and most abundant deposit produced by alcohol in the solution which had been agitated with ether to extract the lactic acid (7), was now very carefully examined.

This deposit contained, in addition to the confused mass of crystals of sulphate of potassa, a number of rectangular tables, which were most abundant in the later portions of the deposit, formed when the alcohol greatly predominated.

9. The mass was treated with warm water, by which it was only partially dissolved; the dark brown solution was evaporated to a small bulk on the water-bath, when it deposited a peculiar tenacious mass, showing no signs of crystallisation. The mother-liquor was evaporated to a syrupy consistence, but no crystals of incite could be obtained, nor did I succeed in eliciting any of the reactions pointed out by Scherer as distinguishing that substance.

10. The residue left by warm water was boiled with water, when it almost entirely dissolved.*

The solution deposited crystals of sulphate of potassa, and the mother-liquor from these gave large crystals of sulphate of soda.

11. The first aqueous extract (9), obtained by treating the deposit with warm water, when saturated with carbonate of baryta, filtered, and evaporated, gave a syrupy brown liquid, which had an alkaline reaction, and was not miscible with alcohol or ether. This liquid was dissolved in water, the solution mixed with alcohol till it became turbid, heated till clear again, and allowed to stand; merely a viscid liquid was deposited.

The alcohol was then distilled off, the sulphuric acid removed by an excess of baryta-water, the baryta precipitated by carbonic acid, and the solution evaporated.

It left a brown viscid residue, nearly free from inorganic matter, very readily soluble in water, yielding a solution which was strongly alkaline to litmus and turmeric; it also now dissolved, though slowly, in alcohol, and was precipitated from the solution on adding dilute sulphuric acid.

On standing for a day or two, this viscid liquid solidified to a

* The small quantity which remained undissolved appeared to be a compound of sulphate of potash with some organic substance; it was dissolved only by nitro-hydrochloric acid.

crystalline mass, which only partly dissolved in alcohol, even on boiling, leaving white prismatic crystals.

Hydrochloric acid dissolved them at once, with evolution of heat.

The whole of the crystalline mass was thoroughly washed with alcohol, which left a brownish white crystalline powder, more of which was afterwards recovered from the alcoholic washings.

This substance dissolved very readily in water; the solution was decidedly alkaline to red litmus, but not to turmeric.

It dissolved very sparingly, even in boiling alcohol, which sufficed to distinguish it from kreatinine.

Ether did not dissolve it.

When heated in a test-tube, it resisted a considerable degree of heat without change, but finally fused, evolved ammonia, and left a very bulky coal. None of the substance sublimed unchanged, proving that it was not sarcosine.

The aqueous solution was not precipitated by alcohol, even on adding sulphuric acid.

When dissolved in a drop of hydrochloric acid, and evaporated upon a slip of glass, no well-marked crystals were obtained; but, on adding a little bichloride of platinum, and again evaporating, very distinct cubes were perceptible.

The concentrated solution of the base in hydrochloric acid was not precipitated by bichloride of platinum.

The hydrochloric solution, evaporated in vacuo, left a gummy mass.

Chloride of mercury (corrosive sublimate) added to the aqueous solution, gave a white precipitate, which coagulated in a curious manner when heated.

(10.36 grs. of this compound, dried in vacuo, lost no more at 212° . Dissolved in nitric acid, the mercury determined as sulphide, gave 58.08 per cent. The chlorine amounted to 11.45 per cent).

Terchloride of gold gave a yellow flocculent precipitate in the aqueous solution.

The crystals suffered no appreciable diminution when dried in vacuo and in the water-oven.*

* Although I have made an ultimate analysis of this base, the circumstances of my having so small a quantity to operate upon, of my not being able to obtain a trustworthy determination of the equivalent number, and, above all, my doubt as to

12. Being desirous of satisfying myself as to the nature of the volatile acids contained in the juice of beef, I examined the acid liquid above alluded to as obtained by distilling the aqueous infusion with sulphuric acid (6).

This liquid was mixed with an excess of baryta-water, evaporated to a small bulk, filtered from the separated carbonate, and further evaporated in vacuo, when it deposited a hard crystalline salt.

17.01 grs. of the crystals, dried in vacuo and incinerated, gave 10.76 grs. carbonate of baryta, representing 49.09 per cent. of baryta.

Butyrate of baryta ($\text{BaO} \cdot \text{C}_4\text{H}_7\text{O}_2$), should have furnished 49.19 per cent.

The properties of the salt also agreed perfectly with those of the butyrate.*

The mother-liquor from the crystals of butyrate of baryta was evaporated to dryness in vacuo.

21.22 grs. of the residue, when incinerated, gave 14.13 grs. carbonate of baryta = 51.7 per cent. of baryta.

Metacetate of baryta ($\text{BaO} \cdot \text{C}_6\text{H}_5\text{O}_2$) would have given 54.1 per cent., so that there is room for the supposition that the salt was a mixture of the butyrate with a little metacetate of baryta, though I was rather inclined, from other circumstances, to attribute the observed excess to a little carbonate of baryta, which the salt was found to contain. I had not sufficient to enable me to

the absolute purity of the small specimen analysed, makes me very diffident in quoting the results, although they appear to agree passably well with those calculated.

I.—5.88 grs. of substance, ignited with soda-lime, gave 23.13 grs. of the double chloride of platinum and ammonium = 1.4508 nitrogen = 24.67 per cent. (The platinum-salt, when ignited, gave 10.17 grs. platinum, instead of 10.22.)

II.—3.69 grs., burnt with oxide of copper, gave 6.20 grs. carbonic acid and 2.18 grs. water; 45.82 per cent. carbon, and 6.56 per cent. hydrogen.

III.—2.24 grs. gave 3.73 grs. carbonic acid, and 1.38 grs. water, representing 45.41 per cent. carbon, and 6.84 per cent. hydrogen.

The mean of these analyses would give the empirical formula $\text{C}_{13} \text{H}_{11} \text{N}_3 \text{O}_5$.

| | | Calculated. | Found. |
|----------|----|--------------|--------------|
| Carbon | 13 | 45.61 | 45.61 |
| Hydrogen | 11 | 6.44 | 6.70 |
| Nitrogen | 3 | 24.56 | 24.67 |
| Oxygen | 5 | 23.39 | 23.02 |
| | | <hr/> 100.00 | <hr/> 100.00 |

* It is worthy of remark that this salt was perfectly anhydrous, although crystallised in the cold; I do not remember that any form of crystallised butyrate of baryta but those with 2 and 4 eqs. Aq. had yet been noticed.

decide the point. When this salt was again dissolved in water, and the solution was evaporated in vacuo, it gave a transparent viscid liquid, which became opaque and solid when briskly stirred, being converted into a mass of minute crystals, which appeared, under the microscope, precisely similar to those of the butyrate. When distilled with dilute sulphuric acid, it furnished a liquid closely resembling an aqueous solution of butyric acid.

13. The crystals which were deposited from the aqueous fluid before distillation with sulphuric acid, on standing for ten or twelve weeks (5), deserve a few remarks.

They were exceedingly heavy, and although they burnt entirely away when heated on platinum, they were insoluble in boiling water, alcohol, and ether.

Under the microscope, they appeared to be four-sided rectangular prisms.

Heated on the water-bath, they fused to minute globules having a crystalline fracture.

Heated on platinum, they evolved a very decided odour of nitrogenised organic matter.

Dissolved on heating with hydrochloric acid; not reprecipitated by ammonia.

Dissolved by potassa, on boiling; the solution was not altered by hydrochloric acid, and gave no dark precipitate with acetate of lead.

Ammonia dissolved it, with some difficulty, on boiling.

Dilute sulphuric acid dissolved it, on boiling.

Concentrated sulphuric acid dissolved it; the solution was not precipitated by water.

Concentrated nitric acid rendered the crystals white and opaque, but dissolved them with difficulty; on allowing the solution to evaporate slowly upon a water-bath, it deposited, on cooling, very lustrous crystals, apparently oblique rhombic prisms. (No oxalic acid was found in the nitric solution.) These prisms became opaque when washed with cold water; they dissolved on heating with water; the solution gave a white precipitate with nitrate of silver which was insoluble in cold concentrated nitric acid, but dissolved on heating, and was deposited again in delicate needles when the solution cooled.

The following are the chief points to which it has been especially desired to call attention by these remarks.

1. That in this particular case, the quantity of lactic acid must

have been so small that even its existence in the juice has not been satisfactorily made out.

2. That, instead of lactic acid, a crystallised acid containing nitrogen has been obtained, though its composition has not been determined.

3. That a crystallised base has been obtained, very rich in nitrogen, and sparingly soluble in alcohol, though readily dissolved by water.

4. That the volatile portion of the acid constituents of the juice of beef consists almost, if not quite, entirely of butyric acid.

5. That there was extracted from the juice an easily fusible crystalline organic substance containing nitrogen, insoluble in water, alcohol, and ether, and yielding a crystalline compound when boiled with concentrated nitric acid.

I have been induced to submit these results to the Society, less by attributing to them any merit in their present incomplete state, than by the hope that I might have thus acted as a pioneer for some investigator with more leisure, who might add an exact description of these substances to the records of chemical science.

I must beg my friend Dr. Miller to accept my thanks for the kind advice which I have received from him in prosecuting these experiments.

XVI.—*On the Fatty Matters of Human Excrements in Disease.*

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It has often been noticed that excessive quantities of fats are voided by the motions in certain diseases; but no attempt having been made to separate these fatty substances from each other, and obtain them in the form of Immediate Principles, I have undertaken this task in one case, by adopting a method of investigation similar to that which I had made use of for the analysis of healthy excrements. The case in question is that of a man who was for a long time my patient at the Westminster Hospital, labouring,

apparently, under disease of the kidneys. From his excessive emaciation, it was evident that the assimilation was very defective, and, with the view of endeavouring to obtain some further insight into the nature of the disease, his *faeces* were submitted to examination. They had the consistence of putty, a yellow grey colour, and a strongly acid reaction. When boiled with alcohol, they formed an homogeneous mass, which, being squeezed in a muslin bag, yielded a turbid alcoholic fluid; this was now filtered through filtering paper, and the insoluble residue exhausted with boiling alcohol. On cooling, an abundant crystalline deposit, quite free from colouring matter, occurred in the solution. In order to analyse the deposit, it was collected on a filter, and the filtrate was left to evaporate spontaneously. I removed the deposit to a flask, and then treated it with ether, until nothing more was dissolved; by so doing, the crystalline mass was divided into a substance insoluble in ether, and one which was soluble in this fluid. The substance insoluble in ether dissolved in hot alcohol, but was sparingly soluble in cold alcohol; the solution had an acid reaction. The crystals were soluble in hot water; but the addition of cold water to the alcoholic solution, induced the formation of a cloudy precipitate, and the fluid gradually became neutral.

This compound fused at a temperature ranging between 100° and 103° C. When the aqueous solution was mixed with hydrochloric acid, the liquid deposited white flakes; these were collected on a filter, and the acid filtrate being evaporated to dryness, left a residue, which did not clear on the application of a strong heat, and was found to consist of nothing but chloride of sodium. The white precipitate being washed with water till the washings ceased to give a precipitate in a solution of nitrate of silver, was treated with ether, when it dissolved, resuming its crystalline form by spontaneous evaporation; the crystals were also soluble in hot alcohol. They fused at 66° C. and reappeared at 64° C. When burnt on a platinum spatula, this substance charred, ignited, and left no residue.

In short, there could be no doubt but that it was stearic acid; consequently, it appeared very probable that the original compound insoluble in ether was the *bistearate* or the *stearate of soda*. The fact was placed beyond doubt by a quantitative analysis of the substance. For this purpose, a sample of the compound, thoroughly exhausted with ether, was dried over sulphuric acid, under the air-pump, until it ceased to lose weight; it was then found to weigh

0·275 grammes. The substance was now dissolved in hot water, (being insoluble in cold water) and decomposed with hydrochloric acid in excess, when an abundant flocculent precipitate of fatty acid occurred. The precipitate collected on a filter, and washed with distilled water (till the washing ceased to produce a haziness in a solution of nitrate of silver), was removed into a weighed watch-glass, to be dried over sulphuric acid under the air-pump. In order to avoid losing a trace of the fatty acid, the filter itself was treated with ether, and the solution evaporated to dryness in a weighed watch-glass, which, when dried under the air-pump, gave only 0·006 grammes of the substance. The whole weight of the perfectly dry fatty acid was 0·259; therefore, 0·275 grammes of the compound submitted to analysis, consisted of

0·259 grammes of stearic acid,
and 0·016 grammes of soda.

0·275

or, 100 parts contained

94·18 of stearic acid,
and 5·82 of soda.

100·00

Chevreul found 100 parts of bistearate of soda to consist of

| | |
|--------------------|---|
| Stearic acid . . . | 94·33 |
| Soda | 5·67 |
| | <hr style="width: 20%; margin: 0 auto;"/> |
| | 100·00 |

Consequently, the substance under examination was *bistearate of soda*.

It is the first time, I believe, that *bistearate of soda* has been extracted directly from the animal body, and, consequently, in the form of an Immediate Principle. Its separation from the other fatty acids is very easy, on account of the circumstance that this compound is insoluble in ether; and it is readily distinguished from the other soaps by its property of crystallising in a concentrated alcoholic solution as soon as the fluid has become cold, whilst the other compounds of fatty acid and soda solidify from their solution in alcohol, in the form of a gelatinous deposit, which

crystallises on standing, after some time has elapsed. Bistearate of soda was first obtained by Chevreul by dissolving 1 part of stearate of soda in 2000 or 3000 parts of hot water, filtering the liquor when cold, washing the deposit, drying it and treating it with hot alcohol; the solution, when cold, deposited *bistearate of soda*.*

In no case have I detected this compound as an Immediate Principle of healthy human evacuations; it is, consequently, a morbid product, resulting, in all probability, from the action of abnormally large quantities of free acids in the intestinal canal: the very acid reaction of the excrements supports this view. Healthy human fæces yield margarate of lime and margarate of magnesia; if they contain any soda or potash soap at all, it must be in very small quantities. Free fatty acids do not exist in healthy human evacuations, unless a comparatively large amount of vegetable food has been taken; and in these cases I have not detected the presence of any bistearate.

The excrements in the present instance yielded not only bistearate of soda, but a considerable quantity of free fatty acids, which most probably depended, as I shall presently show, on the functions of the pancreas and liver being arrested.

The alcoholic filtrate from the bistearate of soda, gave on standing, another crop of crystals, consisting of a mixture of bistearate of soda and of fatty acid. By treating these various deposits with ether, a substance was dissolved which crystallised by spontaneous evaporation, and proved to be a mixture of stearic and margaric acids, the former being in excess. The crystallised deposit possessed the following characters. The crystals occurred under the form of small white masses, exhibiting under the microscope groups of needles radiating from the centre to the periphery. They fused at a temperature of 60°C , which, according to Gottlieb, corresponds to a mixture of eighteen parts of stearic with ten parts of margaric acid; they were soluble in cold ether and in hot alcohol, and insoluble in water; the substance dissolved in potash and could be precipitated in this alkaline liquor by means of hydrochloric acid; when heated on the platina-knife, the crystals fused, ignited, and finally left no residue. These characters are precisely those of the above-mentioned fatty acids; the amount of the mixture at my disposal did not allow of the complete separation of these acids being effected.

* Recherches Chimiques sur les corps gras d'origine animale. Par M. J. Chevreul.

The clear alcoholic fluid being allowed to stand undisturbed for twenty-four hours, yielded another crop of beautifully white glistening crystals. These were submitted to examination and proved to be *margaric acid*, apparently free from stearic acid. These crystals dissolved in ether and hot alcohol, and crystallised from these solutions; the ethereal and alcoholic fluids had an acid reaction; the substance was insoluble in water, but dissolved in aqua potassæ. Hydrochloric acid induced its precipitation from the alkaline liquor. It fused at 53° Cent., and crystallised, on cooling, at 49° , this low fusing point being due probably to the admixture of a small quantity of oleic acid; the crystals occurred in the form of small radiating masses peculiar to margaric acid; they burnt with a fuliginous flame, leaving no trace of ashes.

The occurrence of such quantities of fatty acids in this case being considered in connection with the condition of the body of the patient, is of great interest, not only in a chemical but also in a physiological and pathological point of view. The pancreas of the patient was found, at a *post mortem* examination, entirely disorganised by malignant disease, and it apparently so compressed the duct of the gall bladder that no bile could flow into the intestines. Consequently, the two alkaline intestinal secretions were wanting, and the fatty acids contained in the alimentary canal could not be neutralised. This is an important fact in favour of Bernard's view respecting the properties of the pancreatic juice.

I avail myself with pleasure of this opportunity to acknowledge the valuable aid I have received from my assistant, Dr. Frederick Dupré in these and other investigations.

XVII.—On some of the Products of Oxydation of Chinese Wax.

By G. B. BUCKTON, Esq., F.L.S., F.C.S.

SOME years have elapsed since Gerhardt first pointed out the analogy and connection which exists between the monobasic, so called, fatty acids, and the series of bibasic acids, represented respectively by the formulæ $C_{2n}H_{2n}O_4$ and $C_{2n}H_{2n-2}O_8$.

He showed that by careful fusion with hydrate of potassa,

several members of the one series may be converted into those of the other. Thus, oxalates are well known to yield formiates by dry distillation, whilst by treatment with nitric acid, butyric and stearic acids have been proved to yield succinic acid.

More recently Dr. Hofmann has pointed out the existence of a series of similar bibasic acids which correspond to the monobasic aromatic acids. These substances are likewise produced by the action of oxydation upon the monobasic acids. The bibasic group, corresponding to the aromatic acids, is far from being complete, but the group connected with the fatty acids exhibits at present but two gaps between oxalic and sebacic acids, the terms with four and eighteen carbon being wanting.

There appeared some hope of filling these vacancies, and perhaps of extending the series by studying the action of nitric acid upon some of the fatty and waxy bodies, which have not yet been examined with this view.

Professor Brodie,* in his memoir read before the Royal Society, has already demonstrated Chinese wax to be a fatty ether, compounded of cerotic acid, with its corresponding base ceryl, $C_{54}H_{53}(C_{54}H_{55})O_4$, and that by fusion with hydrate of potash, the ceryl gives up part of its hydrogen and passes by oxydation into cerotic acid.

As therefore little new offered itself in this direction, I have in this paper wholly confined myself to a description of the products eliminated by the action of nitric acid.

The wax was broken into lumps and introduced into a capacious retort, and heated, at first gently, with from four to five times its bulk of acid, which, for this purpose, must be in a concentrated form. The strongest ordinary nitric acid of commerce has a sp. gr. of 1.39 or 1.40, and will be found sufficient for the purpose. A condensing apparatus was attached, but not in such a manner as to permit the more volatile portions to return on the wax, which would have prevented the action of the acid in its full strength. When ebullition commenced, a large quantity of red vapour passed over, and in an hour's time, the contents of the retort frothed much from the increased viscosity of the waxy stratum. After a while, the action calmed, and when the digestion had been continued for three hours, it was arrested, the distillate having been once returned to the retort during the interval.

I have found a close adherence to one mode of operation very

* Phil. Trans. Roy. Soc. 1848. Part I., p. 161.

desirable. A comparatively slight alteration in the density of the acid employed, or an increase in the time of digestion, modifies the results and eliminates products of a simpler character than those desired for study.

After agitating the contents of the retort with a moderate quantity of boiling water, the whole was poured into a beaker and set aside for twelve hours. The upper stratum, which had the consistence of tallow, was removed, and the liquid separated from the greasy flakes which were suspended, by filtration through asbestos. The acid liquid was then concentrated to about $\frac{1}{3}$ of the bulk of the nitric acid originally used, and allowed to stand for twelve hours, after the expiration of which a crust had formed upon the surface, which, when removed from the liquid, was plentifully washed with cold water. The mass was then rubbed to a paste in a mortar, and again washed until the rinsings had but a feeble acid taste.

The washings were added to the first filtrate for subsequent concentration and examination.

From a hot aqueous solution, the new substance crystallises in soft nodular masses, of a snowy whiteness, which are, however, contaminated with an oily substance, very difficult to separate by simple crystallization from water. The mass was therefore placed in paper and subjected to a screw press, and after being thoroughly dried was fused in a porcelain dish. When cold it was powdered and agitated with a little ether, which reduced the quantity, but removed the oily matter. The substance remaining on the filter was pressed and allowed to dry spontaneously. Another crystallisation from water furnished the substance pure.

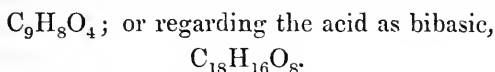
The crystals are very minute, and are but slightly acid to the taste, which character is due to their little solubility in cold water. The aqueous solution easily reddens litmus paper. Hot water dissolves the acid to an almost unlimited extent, and the solution becomes densely white and semifluid on cooling.

The melting point of the dry acid was taken from two separate preparations, one of which liquefied at 114° and the other at 116° . From the fact that a minute trace of moisture depresses the melting point of suberic acid in a marked degree, I am inclined to believe the latter figure to be the most correct. When a film of the melted acid is allowed to cool under the microscope, it crystallises very distinctly and shoots into short needles in all directions. The fused mass, when cold, may be readily reduced to powder under the pestle.

For analysis, a portion of the substance was retained at the melting point until all bubbles of air and moisture had disappeared, and then burnt with oxide of copper.

0.2015 grms. of substance gave
 0.4215 „ carbonic acid and
 0.1575 „ water

From the percentage composition is deduced the formula



This, therefore, represents the acid, hitherto, I believe, unknown, intermediate to suberic and sebacic acids. For comparison I annex the percentages obtained by experiment and those required by theory:—

| Suberic acid. | | | New acid. | | | Sebacic acid. | | | |
|-----------------|----|-------|-----------------|-----|-------------|---------------|-----------------|-----|-------|
| | | | Theory. | | Experiment. | | | | |
| C ₁₆ | 96 | 55.17 | C ₁₈ | 108 | 57.44 | 57.02 | C ₂₀ | 120 | 59.45 |
| H ₁₄ | 14 | 8.04 | H ₁₆ | 16 | 8.51 | 8.68 | H ₁₈ | 18 | 8.91 |
| O ₈ | 64 | 36.79 | O ₈ | 64 | 34.05 | 34.30 | O ₈ | 64 | 31.64 |
| <hr/> | | | <hr/> | | <hr/> | | <hr/> | | |
| 174 100.00 | | | 188 100.00 | | 100.00 | | 202 100.00 | | |

The substance under examination, when strongly heated, partly decomposes and partly sublimes in white vapours, which, although inodorous, exert a painful choking sensation in the chest when inhaled.

This property, which, however, is common to all the known acids in the oxalic series, with the exception of pyrotartaric, has suggested a name.

I propose to call the acid *Anchoic Acid*, and its salts *Anchoates*, from the Greek word *αγγχω*, I suffocate. Apart from the varied constitution of this acid, it will be found to differ both in crystalline appearance, in its solubility in water and in ether, and also in its melting point, from either of the acids immediately preceding and following it.

The salt first analysed was the

ANCHOATE OF SILVER.

This substance is easily prepared by precipitating with nitrate of silver an aqueous solution of anchoic acid which has been previously neutralized by ammonia.

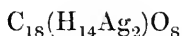
It is white and flocculent, and when dry will bear, without decomposition, a temperature of 120° . It is soluble in dilute acid, but little soluble in water. The dry salt becomes highly electrical when rubbed in a warm mortar.

| | | |
|------|--------|---|
| I. | 0.2650 | gms. dried at 110° when ignited gave |
| | 0.1415 | „ of metallic silver. |
| II. | 0.2075 | „ at 120° gave |
| | 0.1115 | „ of metallic silver. |
| III. | 0.3520 | „ at 120° gave |
| | 0.1890 | „ of metallic silver. |

These numbers correspond to the following percentages*—

| | I. | II. | III. |
|--------|-------|-------|-------|
| Silver | 53.35 | 53.73 | 53.69 |

and to the formula



The mean of the experiments compared with theory is:—

| | Theory. | | Experimental mean. |
|-----------------|-----------|--------------|--------------------|
| C_{18} | 108 | 26.86 | — |
| H_{14} | 14 | 3.48 | — |
| Ag_2 | 216 | 53.73 | 53.57 |
| O_8 | 64 | 15.93 | — |
| | <hr/> 402 | <hr/> 100.00 | |

ANCHOATE OF BARIUM.

An aqueous solution of anchoic acid acts but feebly upon carbonate of barium, and the liquid can only be neutralized by a continued boiling with an excess of base. The neutral salt, however, is readily obtained by substituting hydrate of baryta. The solution, when evaporated on the water bath, forms a pellicle which is at first transparent, but becomes opaque at 100° from the loss of water. It is insoluble in alcohol and in ether, but very soluble in water.

* The percentages of silver in the two nearest allied salts are:—

| | Suberate of silver. | Sebacate of silver. |
|--------------|---------------------|---------------------|
| Silver . . . | <hr/> 55.67 | <hr/> 51.91 |

The dry salt becomes pasty by a strong heat, but does not wholly fuse. It blackens and burns with a smoky flame, leaving a residue of carbonate of barium.

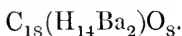
Samples from different preparations were used for analysis.

- I. 0.3920 gms. dried at 110° gave with sulphuric acid
 0.2808 „ of sulphate of barium
 II. 0.3460 „ dried at 115° gave
 0.2513 „ sulphate of barium

representing in 100 parts,

| | I. | II. |
|----------------|-------|-------|
| Barium | 42.12 | 42.68 |

the mean of which closely accords with the formula,



| | Theory. | | Mean of Experiment. |
|-----------------|-----------|--------------|---------------------|
| C_{18} | 108 | 33.43 | — |
| H_{14} | 14 | 4.33 | — |
| Ba_2 | 137 | 42.41 | 42.40 |
| O_8 | 64 | 19.83 | — |
| | <hr/> 323 | <hr/> 100.00 | |

This solution does not exhibit definite crystals, even when concentrated and viewed by a lens.

I have not been able to prove the bibasic character of anchoic acid by an analysis of an acid barium salt. A weighed portion of acid was exactly neutralized with hydrate of baryta and added to a similar quantity of acid. The substance, however, which was obtained by evaporation, was found to give up the whole excess of acid when digested with alcohol, and the neutral salt remained alone in the filter.

This fact accords with the observation of M. Dœpping, who failed in obtaining the acid succinate of barium by a like method.

ACID ANCHOATE OF POTASSIUM.

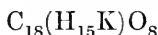
That anchoic acid may be made to combine with either one or two equivalents of base, can be shown by the preparation of the acid potassium salt. The above process of semi-neutralization was adopted, carbonate of potassium being substituted for the barium salt, and the liquid was evaporated on the water-bath to

dryness. The crystalline residue was agitated with a small quantity of cold water, and then filtered from a few flakes of acid, which was, intentionally, in slight excess. The solution concentrated over sulphuric acid gave a colorless salt, which differed in appearance from the neutral anchoate, presenting the form of circular or tubercular grains under the microscope. They are soluble in about three parts of cold water, but exceedingly soluble in hot water. Methylated spirit also dissolves them without difficulty. They are not deliquescent, they have a cooling acid taste, and bear a temperature of 140° without change. They begin to lose their whiteness at 160° , and, when further heated, give off white fumes and burn with a smoky flame and deposit of carbon.

For analysis, the salt was calcined, and afterwards converted into chloride of potassium, by boiling with chloride of ammonium.

0.2634 gms. of substance dried at 110° gave, when ignited,
0.0895 ,, chloride of potassium

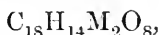
a result which accords sufficiently well with the formula



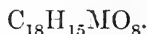
as may be seen by comparing the experimental percentage with that required by the acid and neutral salt.

| Neutral anchoate of potassium. | | | Acid anchoate of potassium. | | | Experiment. |
|--------------------------------|-------|--------|-----------------------------|-------|--------|-------------|
| C_{18} | 108 | 40.90 | C_{18} | 108 | 47.78 | — |
| H_{14} | 14 | 5.30 | H_{15} | 15 | 6.63 | — |
| K_2 | 78 | 29.54 | K | 39 | 17.25 | 17.78 |
| O_8 | 64 | 24.26 | O_8 | 64 | 28.34 | — |
| | <hr/> | <hr/> | | <hr/> | <hr/> | |
| | 264 | 100.00 | | 226 | 100.00 | |

The composition of the neutral anchoates is therefore represented in a general manner by the expression



and the acid anchoates by the formula



The other salts of anchoic acid are so similar in appearance and properties to the sebacates, that a few words only need be said regarding them.

Neutral anchoate of Potassium. This substance is very soluble in water. It gives on evaporation a confused crystalline mass, destitute of regular forms.

Anchoate of Ammonium is very soluble in water and in alcoholic spirit. The solid salt is amorphous and loses ammonia when gently heated.

Anchoate of Sodium is more crystalline than the potassium salt. Sulphuric acid throws down anchoic acid in a solid form, from moderately strong solutions.

Anchoate of Zinc is a white precipitate formed when sulphate of zinc is added to anchoate of potassium.

Anchoate of Copper forms a copious, blue, insoluble precipitate when a neutral anchoate is decomposed by a copper salt. Anchoic acid gives no precipitate under similar circumstances.

Anchoate of Lead. This substance appears in a white bulky form when anchoate of ammonium is treated with acetate of lead. It is quite insoluble in water, but soluble in dilute nitric acid, from which solution anchoic acid is deposited on cooling.

Anchoate of Mercurousum may be obtained by precipitating the corresponding nitrate, by either anchoic acid or any of its soluble salts.

Anchoate of Mercuricum may be obtained by adding a neutral anchoate to a solution of chloride of mercury. It forms a white and curdy precipitate.

Anchoate of Ethyl. When an alcoholic solution of anchoic acid is saturated with hydrochloric acid gas, the liquid rises in temperature and the ether is formed, together with abundance of chloride of ethyl vapour. A moderate heat drives off the excess of hydrochloric acid, and, after washing with water, the ether may be purified by rectification.

It is an unctuous liquid, with rather a pleasant odour, but hot and persistent taste.

It is almost wholly insoluble in water, upon which it floats. It readily mixes with both alcohol and ether. Its boiling point is about 325° .

EXAMINATION OF THE MOTHER LIQUID AFTER REMOVAL OF ANCHOIC ACID. •

This liquid, which also contained the washings from the former acid, was evaporated so as to drive off a further portion of nitric

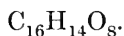
acid, a little water being added from time to time, and the whole being stirred to prevent the substances in solution becoming brown.*

When sufficiently concentrated, a small portion of water was added and the fluid set apart for twelve hours to crystallise. The crop of crystals was removed, washed with a little water, and after draining on a tile, was dried at a gentle heat. Traces of anchoic acid were removed by agitation with a little ether, and afterwards the substance was purified by two crystallisations from water.

The crystals, which were much larger than those obtained from anchoic acid, were also much more soluble in water. Ether, on the contrary, exhibited a less solvent action upon them. They had a strong acid taste, and the dry acid had a melting point of 126° .

| | |
|--------|------------------------|
| 0.1924 | gms. of substance gave |
| 0.3878 | „ carbonic acid and |
| 0.1420 | „ water |

The substance, therefore, was clearly suberic acid, the formula calculated from the percentage being



The numbers required by theory and obtained by experiment are

| Suberic acid. | | | Experiment. |
|-----------------|-------|--------|-------------|
| C_{16} | 96 | 55.17 | 54.93 |
| H_{14} | 14 | 8.04 | 8.19 |
| O_8 | 64 | 36.79 | 36.88 |
| | <hr/> | <hr/> | <hr/> |
| | 174 | 100.00 | 100.00 |

As a check upon the foregoing analysis, a barium salt was prepared from a portion of the acid, and afterwards decomposed by sulphuric acid.

| | |
|--------|----------------------------------|
| 0.3235 | gms. dried at 115° gave |
| 0.2633 | „ sulphate of barium. |

* If the concentration be carried too far, a violent reaction sets in; red vapours are produced, and the mass, if large, is liable to take fire spontaneously.

Suberate of barium $C_{16}H_{12}Ba_2O_8$ contains in 100 parts,

| | Theory. | Experiment. |
|--------------|---------|-------------|
| Barium . . . | 44.33 | 44.42 |

There can, therefore, be no doubt that suberic acid is one of the chief products of the action of nitric acid on Chinese wax. The greater or less amount eliminated depends mainly upon the duration of the action.

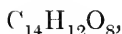
EXAMINATION OF THE LIQUID AFTER THE SEPARATION OF SUBERIC ACID.

This filtrate obviously contained other substances more soluble and less crystalline than either of the two acids above described. By further evaporation and draining the mother liquor from the mass, and by subsequent pressure between paper, a crystalline substance was obtained, which was exceedingly soluble in ether and in alcohol. I could procure only a small portion in a state of purity, finding it very difficult to remove other acid bodies, which had the consistence of tallow.

The sample taken for analysis had a melting point of 110° . By combustion with oxide of copper,

| | |
|--------|------------------------|
| 0.3204 | gms. of substance gave |
| 0.6202 | „ carbonic acid and |
| 0.2226 | „ water. |

indicating the formula,



which is that of pimelic acid, obtained by Laurent from bees'-wax, spermaceti, and other fatty bodies.

Annexed are the percentages required by theory and found by experiment :—

| | Theory. | | Experiment. |
|----------|---------|--------|-------------|
| C_{14} | 84 | 52.50 | 52.46 |
| H_{12} | 12 | 7.50 | 7.70 |
| O_8 | 64 | 40.00 | 39.84 |
| | <hr/> | <hr/> | <hr/> |
| | 160 | 100.00 | 100.00 |

I have not further examined the remaining acids contained in the mother liquid, since it would scarcely repay the tedium and

labour of separating them from each other. Also the fact that adipic and other lower acids have been already obtained by both Malaguti and Laurent from similar sources, made a more extended inquiry in this direction unnecessary.

I have found that no advantage is gained in preparing anchoic and similar acids by substituting cerotic acid for Chinese wax. Cerotic acid is more inert to the action of nitric acid than either ceryl alcohol or the wax itself; and I am inclined to believe that the elimination of these acids is principally due to the decomposition of the ceryl in the wax.

Experiment proves that a prolonged digestion with nitric acid, such as for twenty-four hours, resolves both Chinese wax and cerotic acid into an oily body slightly soluble in hot water. This oil does not appear to yield anchoic acid by further treatment.*

On the other hand, ceryl alcohol, $C_{54}H_{56}O_2$, produces the soluble acids of the class without difficulty.

Before dismissing this portion of the subject, a few remarks may be offered upon the melting points obtained, which, in the case of anchoic acid, is perhaps somewhat different from what we might have expected. It cannot, we think, be doubted that there is a relationship between the composition and the points of liquefaction in these bodies.

There is, however, an apparent anomaly in the various acids of the class. Thus succinic acid, with eight equivalents of carbon, melts at 180° ; adipic, with fourteen of carbon, at 145° ; suberic, with sixteen carbon, at 125° ; anchoic acid, with eighteen carbon, at 118° ; and sebacic acid, with twenty carbon, as high as 127° .

Gottlieb and Heintz† have shown that any two fatty acids may form a mixture with a melting point much lower than that of either of them in a state of purity, an observation which also applies to several alloys. Heintz‡ has even been led to believe in a sort of allotropism in stearin, from its having two constant melting points. As therefore a comparatively minute impurity varies the scale so remarkably, I think the fusing points, by themselves, can be little relied upon as a distinctive character.

* I have only slightly examined the nature of this oil. It is heavier than water and obviously is a mixture of several bodies, which decompose at a temperature below that at which they can be distilled *per se*.

† Bericht der Akad. der Wiss. zu Berlin, 1854, p. 207. Chem. Gazette, vol. xii p. 373.

‡ Poggendorff Annalen, vol. xciii. p. 431.

ON THE VOLATILE ACIDS PRESENT IN THE DISTILLATE FROM
CHINESE WAX AND NITRIC ACID.

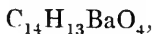
When the red vapours which are abundantly disengaged at the commencement of the reaction are passed through a condenser, a bright emerald green liquid is obtained, upon which a few drops of a highly volatile oil float, having a pleasant odour and peculiar aromatic taste. It was too small in quantity for close examination, but as it distilled unchanged from weak potash it might have been one of the higher alcohols. The green colour of the distillate was very evanescent, and appeared to be due to traces of the oil (which Mr. Brodie states may be extracted in small quantity from Chinese wax), being acted upon by hyponitric acid. Messrs. Boudet and Fauré have shown that a variety of tints may be produced by the combination of hyponitric acid with different fatty bodies.

During the early stages, whilst little nitric acid passes over, a distinct odour of hydrocyanic acid is perceptible, but as the heat is raised it disappears, and gives place to a strong rancid smell of butyric acid. The first distillate was placed in a retort, and again distilled, until nitric acid began to pass somewhat freely. The second distillate was then filtered from a small quantity of oil which floated, and neutralized with carbonate of barium, the nitrate of barium being parted by crystallisation. The mother-liquor was carried nearly to dryness on the water-bath, and digested with alcohol, which separated a small quantity of caprylate of barium.

The two next crops of crystals which appeared from spontaneous evaporation were removed and purified by recrystallisation.

0.2528 gms. of substance gave
0.1500 „ of sulphate of barium,

proving this salt to be cœnanthylate of barium, the formula of which is



and requires

| | Theory. | Experiment. |
|------------|---------|-------------|
| Barium . . | 34.16 | 34.53 |

Although the number obtained is a little high, the salt cannot be confounded with that next in the series. Caprylate of barium is quite insoluble in alcohol. With dilute sulphuric acid an oil was disengaged, which was soluble in an excess of water.

The mother-liquor from the cœnanthylate of barium, gave, on further evaporation, a transparent pellicle, which was also analysed. The substance was dried at 105° , and the amount of barium, estimated in the usual manner, was found to accord with that required for anhydrous butyrate of barium, within five-tenths of a per cent.

As I had plenty of the salt at my disposal, it was distilled with dilute sulphuric acid, and the acid distillate was partially neutralized with potash and again distilled. The condensed liquid which had the well known odour of butyric acid, was neutralized with ammonia and precipitated with a solution of nitrate of silver.

0.3094 gms. when ignited, gave
0.1710 „ of reduced silver.

The percentage composition is almost identical with that required by the formula

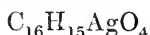


| | Theory. | Experiment. |
|----------------------------------|---------|-------------|
| Silver in butyrate of silver . . | 55.38 | 55.34 |

Lastly, the oil separated by filtration from the distillate was examined. It had all the properties of caprylic acid. It was distilled with water, the vapour of which carried over a sufficient quantity to form a silver salt.

0.4404 gms. dried in vacuo, gave
0.1890 „ of reduced silver,

which corresponds to the formula



| | Theory. | Experiment. |
|-----------------------------------|---------|-------------|
| Silver in caprylate of silver . . | 43.02 | 42.91 |

I am disappointed not to be able to prove pelargonic acid to be one of the products of decomposition of Chinese wax by nitric acid. The fact that acetic acid may be transformed into oxalic acid, and butyric into succinic, would lead us to expect, that pelargonic acid, by assuming oxygen and eliminating water would similarly yield anchoic acid. The list of products, however, is by no means complete, and probably a careful separation of the fatty

mass which is insoluble in water, and which remains after digestion with nitric acid may bring it to light.

In conclusion, I may express a doubt as to pyrotartaric acid being really a member of the series $C_{2n}H_{2n-2}O_8$. From its well known constitution, several chemists have included it in the group, yet its general properties show but little accordance with those of either succinic or adipic acids between which it is placed. If we consider its different mode of production, its fluidity at so low a temperature as $10^{\circ}C$., its volatility without decomposition, and the non-irritability of its vapour when inhaled—characters the reverse of those exhibited by the rest of the series, there is room to believe it to be only a polymeric body, and that the true term is still a desideratum.*

* M. Schlieper seems to have obtained an acid with the composition of pyrotartaric, by acting on sebacic acid with nitric acid. The reaction, however, has failed in the hand of M. Bouis, who simply obtained succinic acid.

Ann. der Chem. LXX. 121, and Gerhardt's *Traité de Chem.* vol. 2, p. 64.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

Anniversary Meeting,—March 31, 1857.

Dr. MILLER, President, in the Chair.

The following Report was read by the President :—

REPORT OF THE PRESIDENT AND COUNCIL.

THE past year has been an important one in the history of the Chemical Society, since, during that period, the Society has become more intimately associated with the Royal Society, and has received apartments from Government in Burlington House, conjointly with the Royal and Linnæan Societies.

It is well known to a large number of our Fellows, that, for some years past, the principal scientific bodies in London have been pressing upon the attention of the Government the importance of the juxta-position of these bodies in a convenient and central locality; and, as result of these efforts, the Government, last spring, entered into communication with the Presidents of the learned Societies then located in Somerset House, offering them rooms in Burlington House in exchange for those which they then held. The Geological and Astronomical Societies considered that the accommodation they already possessed was preferable to that offered at Burlington House, and declined the proposal. Application was then made by the Royal Society to the Government for enlarged accommodation for themselves, and for the Chemical and Linnæan Societies; in reply to which application the following letter was addressed by the Secretary of the Treasury to the President of the Royal Society :—

*Treasury Chambers,
22nd May, 1856.*

“MY LORD,—I am directed by the Lords Commissioners of Her Majesty’s Treasury to acquaint your Lordship, with reference to the views set forth in your letter to the Duke of Argyll of the 30th ult., which has been laid before this Board, that Her Majesty’s Government are not at present in a position to enable them to state any definite views with respect to the project for the juxtaposition of the principal Scientific Societies in a building to be erected in a convenient and central locality.

“I have to state that their Lordships are, however, prepared so far to concede to the views advanced by your Lordship on behalf of a large number of persons connected with science, as to allow the temporary location of the Linnæan and Chemical Societies, in conjunction with the Royal Society, in the present building of Burlington House, on the following conditions, viz.—

“1. That the removal of the Royal Society from Somerset House shall not prejudice the position of the other Societies located in that building, in regard to the terms on which they are permitted to occupy their present apartments.

“2. That the Royal Society shall be put in possession of the main building of Burlington House, on the understanding that they will, in communication with the Linnæan and Chemical Societies, assign suitable accommodation therein for those bodies.

“3. A common Library to be formed for the use of the three Societies, on the understanding that suitable arrangements shall be made for the admission thereto, for purposes of reference and study, of men of letters and science, on orders given by Fellows of the three Societies.

“4. The Societies to be allowed the use of the Hall which it is proposed to construct in the West Wing of Burlington House, at such times as it may not be required by the Senate of the University of London, it being distinctly understood that this permission is to be so exercised as not in any way to interfere with the convenience of the University.

“5. The Collection of Portraits belonging to the Royal Society to be hung on the walls of the proposed Hall, and to be open to the inspection of the public, under such regulations as may be convenient, and subject especially to the proviso in the preceding clause.

“ 6. That the adoption of this temporary arrangement shall not in any respect be held to weaken the claim of the Royal Society to permanent accommodation.

“ I have the honour, &c.,

“(Signed) JAMES WILSON.

“ *To the President of the Royal Society.*”

Upon the receipt of this letter some further communications passed between the President of the Royal Society and the Secretary to the Treasury; and at a Meeting of the Council of the Royal Society, held on the 30th of May, 1856, the President stated, that he had intimated to the Secretary of the Treasury that, in his opinion, the Council would understand the third condition in the foregoing letter as implying the mutual access to the three Libraries by the Fellows of the three Societies, for the purposes of reference and study, but not as altering in any respect the ownership or custody of the several Libraries; and that in future, as heretofore, the loan of the books of any of the three Libraries should be confined to the Fellows of that Society to which they belong.

The President further stated, that Mr. Wilson assented to the above explanation of the minute, so far as it relates to the formation of a common Library.

In conformity with the instructions contained in the letter from the Secretary of the Treasury, communications were entered into with the Presidents of the Chemical and the Linnæan Societies, and the following minute of the Council of the Royal Society was communicated to the President and Council of the Chemical Society:—

*Extract of Minutes of the Council of the Royal Society,
December 18, 1856.*

“ The Secretary presented the following report of the proceedings of the Committee appointed to carry out the arrangements required for the removal of the Society to Burlington House.

“ ‘ At a Meeting of the Committee appointed to carry out the arrangements required for the removal of the Society to Burlington House, held on the 5th December, 1856,

“ ‘ *Present—*

Major-General SABINE, Treas. and V.P., in the Chair.

Mr. Bell, President of the Linnæan Society.

Sir Benjamin Brodie.

Dr. Carpenter.

Dr. Miller, President of the Chemical Society.

Dr. Sharpey.

Mr. Stokes.

“ ‘The Meeting was also attended by Mr. Bennett, Secretary of the Linnæan Society, and Dr. Playfair, who were present by invitation.

“ ‘Resolved,—That as the Royal Society has now been put in possession of the Main Building of Burlington House, the undermentioned apartments be assigned to the Linnæan and Chemical Societies, in accordance with the arrangement already determined on in communication with these Societies, and explained by the President at the Meeting of the Royal Society on the 3rd of June last.

“ ‘To the Linnæan Society :—

“ ‘The Attic Story.

“ ‘The Ball Room and Room adjoining on the North side of the house.

“ ‘The two front rooms on the Ground Floor in the east end of the building.

“ ‘The Wine Cellar in the Basement for a coal cellar.

“ ‘To the Chemical Society :—

“ ‘Two back rooms with Ante-room on the Ground Floor in the east end of the building.

“ ‘The Beer-cellar in the Basement for a coal cellar.

“ ‘The Chemical Society to have the use of the Linnæan Society’s eastern room on the Ground Floor as a Council Room.

“ ‘The three Societies to have the use of the Servants’ Hall as a Kitchen.

“ ‘Mr. Bell, Dr. Miller, and Mr. Bennett, as representing the Linnæan and Chemical Societies, specially intimated their assent to the arrangements here specified.

“ ‘Resolved,—That this report be approved, and the recommendations of the Committee adopted.’ ”

At the closing Meeting of last Session I took the opportunity of stating, that these offers had been acceded to on the part of the Council of the Chemical Society, and that preparations would be made for the removal of the Society to their new apartments

at as early a period as was practicable. The Council were in hopes that it might have been possible to hold the present Anniversary Meeting in Burlington House, but it was found that this could not be done without incurring considerable expense in preparing temporary fittings. There can, however, be no doubt that all the arrangements will be completed in time for the opening of the next Session in the November of the present year.

The Council cannot forbear congratulating the Society upon the manner in which the Fellows generally have testified their interest in the proposed removal; the liberal manner in which they have subscribed towards the expenses incurred for fitting up their new apartments, will, it is expected, render it unnecessary to trench upon the ordinary funds of the Society upon this occasion.

Mr. Delarue, who has kindly undertaken the office of Treasurer to the Removal Fund, reports that a sum of 327*l.* 7*s.* 6*d.* has been subscribed for the purpose above stated, and that of this 197*l.* 11*s.* has already been paid to the account of the Society.

The Council are glad to be able to congratulate the Society on its steady progress, and on the improvement in its finances since the corresponding period of last year.

The present number of Fellows, as compared with the number at the last Anniversary Meeting, is as follows:

| | |
|--|-----|
| Number of Fellows on March 30, 1856 | 256 |
| Fellows elected since that date | 22 |
| Do. resigned | 9 |
| | — |
| Increase | 13 |
| | — |
| Present number of Fellows | 269 |
| | — |
| Number of Associates on March 30, 1856 | 9 |
| Associates elected since that date | 6 |
| Do. deceased | 1 |
| | — |
| Increase | 5 |
| | — |
| Present number of Associates | 14 |
| | — |

| | | | |
|---|---|---|----|
| Number of Foreign Members on March | | | |
| 30, 1856 | | | 20 |
| Foreign Members elected since | 4 | | |
| Do. deceased | 1 | | |
| | | — | |
| Increase | 3 | | 3 |
| | | — | |
| Present number of Foreign Members | | | 23 |
| | | | — |

Papers read at the Meetings of the Chemical Society, between March 30, 1856, and March 31, 1857 :—

- “Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre :” by Messrs. Abel and Bloxam.
- “On New Methods for the Estimation of Minute Quantities of Nitric Acid and Ammonia :” by Mr. J. T. Way.
- “Note on a New Method of Making Ferricyanide of Potassium, and on a Paracyanogen Compound :” by Dr. Lyon Playfair.
- “On the Sulphovimates, and on Amylo-phosphoric Acid and the Amylo-Phosphates :” by Dr. F. Guthrie.
- “On Lophine :” by Messrs. Goessmann and Atkinson.
- “On the Temperature of the opposite sides of a Bismuth Joint while traversed by a Hydro-electrical Current :” by Mr. Richard Adie.
- “On the Analysis of a Meteoric Stone from the Desert of Atacama :” by Mr. Frederick Field.
- “On the Decomposition, by Heat, of native Oxichloride of Copper, or Atacamite :” by Mr. Frederick Field.
- “On Cadmium-ethyle :” by Mr. J. A. Wanklyn.
- “Description of a self-acting Washing-bottle :” by Mr. W. S. Clarke.
- “On a Coal-gas Carbon and Nitric Acid Voltaic Battery :” by Messrs. J. L. and L. Wheeler.
- “On the Analysis of the Iron used in English and Foreign Ordnance :” by Mr. F. A. Abel.
- “On the reciprocal Precipitations of the Metals :” by Dr. Odling.
- “On a new series of Organo-thionic Acids :” by Mr. John T. Hobson.

- "On a new Volumetrical method for the Determination of Copper:" by Mr. E. O. Brown.
- "On the Action of Light upon Chloride of Silver:" by Dr. F. Guthrie.
- "On Compounds obtained by the action of Anhydrous Sulphuric Acid on the Chlorides of Hydrogen, Ethyl, and Methyl:" by Mr. R. Williamson.
- "Note on the action of Bichloride of Carbon on Ethylate of Potash:" by Mr. F. B. Lockwood.
- "On some Thermo-Electrical Properties of the Metals Bismuth and Antimony, when used as single elements:" by Mr. Richard Adie.
- "On the Saponification of Resin:" by Mr. A. G. Anderson.
- "On a Compound obtained by the action of Fuming Sulphuric Acid on Chloride of Phenyl:" by Mr. L. Hutchings.
- "On the Composition of Wheat-Grain and its Products in the Mill, with some Observations on Bread:" by Messrs. Lawes and Gilbert.
- "Notes on Alum in Bread, and its detection:" by Mr. E. H. Hadow.
- "On the Use of the Prism in Qualitative Analysis:" by Dr. J. H. Gladstone.
- "On the Valuation of Nitre:" by Messrs. Abel and Bloxam.
- "On the Thermo-Electric Properties of various Metals in reference to the Direction in which Heat and Electricity cross their Joints:" by Mr. Richard Adie.
- "Note on Crystallised Binoxide of Tin:" by Mr. Abel.
- "On the Temperature of Charcoal while traversed by an Electric Current:" by Mr. Richard Adie.
- "On some remarkable circumstances tending to disguise the presence of various Acids and Bases in Chemical Analysis:" by Mr. John Spiller.

Discourses have been delivered,

- "On Chemistry as applied to the Manufacturing Branches of the War Department:" by Mr. F. A. Abel.
- "A Report on recent Patents connected with the Reduction and Purification of Iron, and its Conversion into Steel:" by Mr. F. A. Abel.

It has not been usual for the President, at the anniversary meetings of this society, to present any sketch of the progress which our science has made during the past year, and I shall therefore not attempt any innovation upon established custom. It is, however, a matter of high congratulation that, both in the departments of organic and of inorganic chemistry, the advances which have been made have been of high interest and importance. I only need to allude to the discovery of allylic alcohol and its derivatives, which we owe to one of our own Fellows, and to other chemists among our nearest neighbours; I need but to mention Wurtz's brilliant discovery of the biatomic alcohols, of which glycol is the type; or to point to Béchamp's interesting researches upon the production of urea by the oxidation of the albuminous principles, to shew that the progress of organic chemistry has kept pace with its importance: and it is scarcely requisite to recall the experiments of Deville upon aluminum, upon silicic acid, and of the same active chemist, in conjunction with Wöhler, upon boron, and with Caron upon magnesium, to shew that inorganic chemistry has not lacked its share in solid and brilliant advances.

One of our fellows, Mr. Perkin, has afforded me the opportunity of bringing before you the results of a successful application of abstract science to an important practical purpose, as he has succeeded in obtaining from aniline a colour which rivals archil in brilliancy, and equals indigo in solidity and durability. Specimens of this dye stuff are now upon the table, and it will be seen that its application to silk in particular furnishes results of great delicacy and beauty.

Science has sustained a severe loss in the death of M. Charles Gerhardt, who expired after an illness of only two days, on the 19th of August, 1856, at the age of 40, just as he had completed his great work on Organic Chemistry. Charles Gerhardt was the son of M. Paul Gerhardt, of Berne, and of Madame Henrietta Weber. In the year 1844 he married the youngest daughter of the late Dr. James Sanders, of Edinburgh. He was elected a foreign member of this Society in the year 1852, and communicated to its transactions two papers on the anhydrous acids in the same year. The following notice of this distinguished man is from the pen of his intimate friend, M. Cahours:—

“Charles Frederic Gerhardt, who has been so recently snatched from science by a premature death, was born at Stras-

bourg, on the 21st of August, 1816. He commenced his studies at the Protestant Gymnasium of this town, and continued them during the course of the years 1831 and 1832 at the Polytechnic School of Carlsruhe. It was in this institution, whilst attending the lectures of Professor Walchner, that a taste for chemistry was first awakened in the mind of Gerhardt. His father, who was the proprietor of a manufactory of chemical products, was delighted to witness this promise in his son, and endeavoured to strengthen his inclination in this direction. He considered the future career of his son as definitely fixed, and expected that he would certainly maintain and extend the reputation of the firm. Young Charles was therefore transferred to Leipzig, to the establishment of M. Shieber. Here he followed with great interest the lectures of M. Erdmann, whilst his zeal and intelligence acquired for him the affection of the Professor. The able lectures and the fatherly kindness of the teacher developed in the ardent and expansive disposition of the pupil an irresistible passion for questions of speculative chemistry.

"Nevertheless, Gerhardt, on his return home, from respect and attachment to his father, endeavoured to realize his wishes. Vain was the attempt! The requirements of commerce, the monotonous and inglorious routine of business, were repulsive to his independent spirit and to his ardent soul. Gerhardt dreamed of a higher destiny. Filial obedience, the prospect of certain success, admonition, remonstrance, all failed to subdue his thirst for instruction and for renown. Severity succeeded no better. To the wise foresight, and to the stern resolution of his father, Charles opposed the headstrong will of youth and the flights of passion. A rupture was inevitable, and it was not long before it occurred. Gerhardt enlisted in a regiment of Chasseurs. It was an excusable piece of folly, the imprudence of a youth of nineteen.

"Soon, however, notwithstanding the indulgence of his colonel, who allowed the new recruit to keep his candle burning after curfew for the purposes of study, notwithstanding the sympathy which he acquired by his unusual amount of information and his good conduct, Gerhardt found a military life insupportable. After a period of three months' service, thanks to the generosity of a friend, who advanced him the requisite sum of money, he purchased his discharge and quitted the army.

"At length he was free! and at length he was in a position to follow his favorite studies without let or hindrance.

"He immediately set out for the laboratory of Giessen, which Liebig then directed with so much *éclat*; and here under the eye of this great master he worked for eighteen months. This was all he needed to qualify him for acting as a teacher in his turn. In 1838 he arrived in Paris, where he was received by M. Dumas with an affection which never wavered. Here he resided, giving lectures and instruction in chemistry. It was at this period that I formed his acquaintance. I was *préparateur* to M. Chevreul; we saw each other frequently; we exchanged ideas with each other; and soon afterwards I obtained from my illustrious master permission for him to work in the laboratory of the Jardin des Plantes. It was there that we commenced together our researches on the essential oils, particularly on the compounds of cuminic acid; researches which he afterwards extended to a number of other essences.

"In 1844, on the recommendation of M. Thénard,* the post of Professor of General Chemistry in the Faculty of Sciences, at Montpellier, was given to Gerhardt. The new professor seriously addressed himself to his work. Intent upon simplifying the study of chemistry, he introduced into his course the new views developed in his '*Précis de Chimie Organique*,' which he published about this time. Already in this work we have sketched the idea of *series* which Gerhardt at a later period developed with so much success.

"But the business of teaching was not sufficient to satisfy the zeal and activity of so ardent a worker. In 1845, Gerhardt, conjointly with Laurent, commenced the "*Comptes rendus des Travaux de Chimie publiés en France et à l'étranger*." Carried away by his love for science, he did not limit himself to giving extracts of these labours; he thought it his duty to attempt to estimate their value. From an examination of the formulæ given by these authors, from a discussion of their value, and from a comparison of these formulæ either with those of the compounds which they form or with the products of their metaprorphoses, he was often led to modify them, and his alterations were almost always confirmed by subsequent experiments. This occurred,

* Dr. Sanders, the brother-in-law of Gerhardt, states that it was to Dumas that Gerhardt was indebted for his chair at Montpellier; and that his subsequent appointment at Strasbourg was due to Thénard, on which occasion the veteran chemist, on taking leave of him when he set out for Strasbourg, said to him, "*Rappelez-vous, M. Gerhardt, quand vous serez vieux et que vous aurez de pouvoir, de protéger toujours les jeunes gens qui travaillent. C'est encore une manière de se rendre utile à la science !*"

for example, for glycocine, leucine, for melam and its various derivatives, and in numerous other cases.

"Still this in his opinion was not doing enough for the progress of chemistry. Isolated from personal communication with men of science, forced even by the nature of his course to limit his ideas within too narrow a space, Gerhardt quitted Montpellier. In 1848 he abandoned his post as professor to come to Paris, and founded, at his own risk, a laboratory where he might follow out uninterruptedly his theories to their realization. It was in a small house in the Rue Monsieur le Prince that he established, between the years 1849 and 1855, in successive memoirs, his notion of series, of homologous series, and the theory of types. It was there that he gave to the scientific world his remarkable researches upon the anhydrous acids and the amides.

"Starting with the numerous and varied facts with which, during the last thirty years, organic chemistry has been enriched, searching with indefatigable ardour through the various memoirs, arranging all the facts, correcting by his own experiments, or by those which he called forth in others, the formulæ which appeared to be doubtful, Gerhardt has established simple theories, which not only cement known facts with each other, but which anticipate a large number of others, and which lead with certainty to discoveries which they clearly indicate. It is thus that by referring all the oxides and all the oxyacids to the type of water, he has enabled the generation of these products to be easily understood; whilst at the same time he has established a simple classification which the mind seizes upon with facility, and which remains deeply engraven upon the memory.

"In giving to the formulæ which represent the composition of a body a value which is not regarded as absolute, in considering them only in some measure as equivalents of composition (a fertile idea first developed by M. Chevreul in his "General Considerations on Organic Analysis"), and in introducing into science the idea of series, Gerhardt has given to chemistry a progressive direction which has earned for its author a high claim upon the gratitude of the true friends of science, and have acquired for him an elevated position in the learned world. All his ideas and his discoveries are developed in his "Treatise on Organic Chemistry," which forms a resumé of his doctrines and an important monument of modern science. He had just completed the revision of the last proof, and had put the finishing touch to his work, and he was rejoicing, as he said in a letter to me written a few days before his lamented end, in the thought of returning to his laboratory

with the view of pursuing new researches, when he was surprised by the hand of death.

“Melancholy lot! After having, by dint of labour and of success, regained the affection of his father, after having won, by his admirable researches, the sympathy of the eminent philosophers whom he formerly in pointed controversy had most wounded, Gerhardt was beginning to enjoy the fruits of his labours, and, perhaps, to forget the painful experience of his past career. These brilliant acknowledgments authorized him to believe that he had rendered important services to chemistry. Nominated in 1855, (thanks to the friendly exertions of M. Dumas), Professor to the Faculty of Sciences at the Ecole Supérieure de Pharmacie, of Strasbourg, he had just received the diploma of corresponding member of the Academy of Sciences in Paris. Freed at length from all anxiety (perhaps for the first time in his life), he enjoyed a lively satisfaction in his position, and meditated new labours, when, exhausted by a struggle too long and too severe, he sank in the moment of triumph and of reward!”

Robert Murray was born at Athy, in Ireland, Sept. 17th, 1798. His father was an officer in the Princess of Wales' Light Dragoons, serving in Ireland during the rebellion.

When fourteen years old, he was apprenticed to Mr. John Newman, the philosophical instrument-maker of Lisle-street, Leicester-square, and afterwards of Regent-street.

For forty-three years he remained in Mr. Newman's service. During this time he became acquainted with all the scientific men of London. He assisted Sir Humphry Davy, Professors Faraday, Wheatstone, Daniell, and Brande, in preparing courses of lectures at the Royal Institution and at King's College. For many years, he also assisted in keeping meteorological observations for the Royal Society at Somerset-house.

His skill and inventive genius were not limited to helping others only, for in 1841 he received the silver medal of the Society of Arts for the invention of a process for taking Voltatype impressions from non-conducting substances by means of a thin coating of plumbago.

Latterly he entered into partnership with Mr. V. Heath as philosophical instrument-makers, of 43, Piccadilly, where he died in the 59th year of his age.

A stone was erected at the Brompton Cemetery to his memory by a few of his scientific friends.

De.

ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY.

Cr.

| 1856. March 31. 1857. March 31. | To Balance from last Account | £ 94 14 6½ | s. 14 | d. 6½ | 1857. March 31. | By Payment of One and Three-quarter Year's Salary to Librarian..... | £ 26 5 0 | s. 5 | d. 0 |
|--|---|---------------|----------|----------|--------------------|---|-------------|---------|---------|
| " | " Subscriptions since received | 335 1 0 | 1 | 0 | " | " ditto of One Year's Rent to Mr. Pepper, of the Royal Polytechnic Institution, including Servants' attendance..... | 130 0 0 | 0 | 0 |
| " | " Admission Fees from Twenty-two Now Members | 44 0 0 | 0 | 0 | " | " ditto of One and a-quarter Year's Salary to Editor of Journal | 62 10 0 | 10 | 0 |
| " | " Compositions in lieu of future Subscriptions | 4 10 0 | 10 | 0 | " | " ditto to H. Baillière for Publishing ditto.. | 94 3 0 | 3 | 0 |
| " | " Half-Year's Dividend on £150 3 per cent. | 0 12 0 | 12 | 0 | " | " ditto for Books and Periodical Publications | 35 8 0 | 8 | 0 |
| " | " Consols, due 5th January last, and Half-Year due 5th July last..... | 20 0 0 | 0 | 0 | " | " ditto for Printing | 12 13 9 | 13 | 9 |
| " | " Proceeds of Sale of Memoirs, No. 1 to 7... | 20 0 0 | 0 | 0 | " | " ditto for Tea and Coffee | 16 0 3 | 0 | 3 |
| " | " One Year's Rent for use of Rooms by the Meteorological Society..... | 20 0 0 | 0 | 0 | " | " ditto for Petty Cash, Postage Stamps, &c.. | 4 5 8 | 5 | 8 |
| " | " One Year's ditto by Ethnological Society.. | | | | " | " ditto for Cavendish Society Subscription, 1856..... | 1 1 0 | 1 | 0 |
| | | | | | " | " ditto to Imperial Gas Company for One Year's Gas..... | 1 10 6 | 10 | 6 |
| | | | | | " | " ditto to John Bayley for Appraising Furniture | 5 18 6 | 18 | 6 |
| | | | | | " | " ditto to John Pursey for Carpenters' Work | 1 11 6 | 11 | 6 |
| | | | | | " | " ditto to Collector for Poundage..... | 18 6 0 | 6 | 0 |
| | | | | | " | " Balance carried to his debit in new Account | 139 4 4½ | 4 | 4½ |
| | | £ 548 17 6½ | | | | £ | 548 17 6½ | | |

London, 31st March, 1857.

R. PORRETT, Treasurer.

Examined and found correct,

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XVIII.—*Contributions towards the History of Thialdine.*

BY A. W. HOFMANN, LL.D., F.R.S.

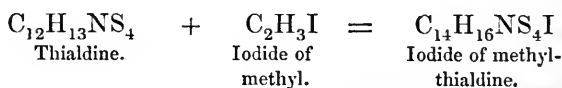
RESEARCHES into the behaviour of several organic bases with bisulphide of carbon, which I intend to lay before the Society at a later period, have led to some experiments with thialdine, the results of which I may be allowed briefly to state, since they are but loosely connected with the principal object of that inquiry.

It appeared of interest to gain some insight into the constitution of thialdine, which is the prototype of an important class of alkaloids containing sulphur. To what group of bases does this body belong? Is it a primary, a secondary, or tertiary base? What shape does its formula assume when referred to ammonia? The favourite method of questioning bases by means of iodide of methyl promised to furnish some elucidation of this subject.

Thialdine, dissolved in iodide of methyl to which conveniently its own bulk of ether has been added, furnishes after twelve hours a solid crystalline mass, which may be readily freed from adhering thialdine by washing with ether and crystallising from alcohol. Ebullition of the mixture, or exposure to heat under pressure in sealed tubes, for the purpose of accelerating the reaction, must be avoided; the mass in this case becomes brown, and is rapidly resinized in consequence of deeper alterations.

With iodide of ethyl, thialdine exhibits exactly the same deportment as with iodide of methyl; the crystalline compound, however, forms more slowly. On the other hand, weeks are required to produce the corresponding amyl-compound with iodide of amyl.

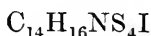
The crystalline compound produced by means of thialdine and iodide of methyl is the iodide of a methylated base, generated, as proved by analysis, by the union of equal equivalents of the two bodies.



An analysis of the crystals gave the following results :

0.3455 grm. of substance burnt with chromate of lead gave :
0.3407 grm. of carbonic acid, and
0.169 grm. of water.

The formula



requires the following values :

| | Theory. | | Experiment. |
|--|---------|--------|-------------|
| 14 eq. of Carbon . | 84 | 27.53 | 26.92 |
| 16 eq. of Hydrogen . | 16 | 5.25 | 5.44 |
| 1 eq. of Nitrogen . | 14 | 4.59 | — |
| 4 eq. of Sulphur . | 64 | 20.98 | — |
| 1 eq. of Iodine . | 127 | 41.65 | — |
| <hr/> | | | |
| 1 eq. of Iodide of Methyl-thialdine | 305 | 100.00 | |

The deportment of the new iodide resembles that of the iodide of tetramethyl-ammonium and the analogous iodides which I described some years ago. Insoluble in ether, soluble in alcohol, and precipitated from this solution by ether in the crystalline state; soluble in water, with an acid reaction, and separated from it again unchanged by potassa in the cold, this substance exhibits

in general all the characters which distinguish the iodides of the so-called ammonium-bases.

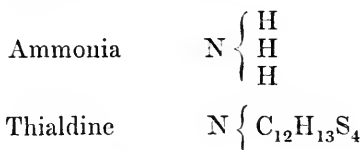
Some deviations, however, must not pass unmentioned. The solubility of the compound is somewhat less than might be expected. Treatment with cold potassa, it is true, does not affect the iodide; but ebullition with potassa gives rise to decomposition, whilst iodide of tetramethyl-ammonium may be recrystallized from a most concentrated boiling solution of the alkali. The action of potassa upon iodide of methyl-thialdine induces, however, by no means the separation of a definite volatile compound, of a methyl-thialdine, but effects a thorough destruction of the body, which is rapidly converted into a brown resinous substance possessing in a high degree the odour of aldehyde. From this substance, which bears a close resemblance to aldehyde-resin, crystals of the unchanged iodide are frequently deposited on cooling; altogether, it appears to be rather the result of the action of heat than of the alkali. When thialdine is strongly heated with iodide of methyl, a brown substance of perfectly similar properties is formed; in fact, thialdine itself, as pointed out by its discoverers, although entirely volatile, cannot be exposed to a high temperature without decomposition.

The great mobility of the elements in thialdine, and especially the large amount of sulphur which it contains, afforded but little hope of successfully submitting the new iodide to the experiment with oxide of silver, which is so characteristic of the ammonium-bases. On adding oxide of silver to the aqueous solution of this body, which, as already remarked, possesses an acid reaction, iodide of silver is formed and the liquid assumes at once a markedly alkaline reaction; but since the almost simultaneous formation of sulphide of silver, and a powerful evolution of aldehyde, sufficiently indicate the complete destruction of the compound, and since experiment exhibits the presence of ammonia in the liquid, it is impossible to decide whether the alkaline reaction, observed in the moment of decomposition, is due to the liberation of an ephemeral ammonium-base, or to its product of decomposition.

The facility with which the base is decomposed, has prevented me from examining any compounds of this body. I should have liked to analyze a platinum- or a gold-salt, but was unable to produce these salts. On adding nitrate of silver to an aqueous solution of the iodide, however diluted, a beautiful yellow precipitate of iodide of silver is obtained, which rapidly turns brown,

and ultimately black, sulphide of silver being formed; in addition the glass vessel is often coated with a mirror of reduced silver, obviously the effect of the liberated aldehyde.

The preceding experiments, which, owing to the peculiar properties of thialdine, are less conclusive than I could have wished, nevertheless appear to show that thialdine belongs to the tertiary bases, that it is a nitrile base.



To the complex molecule $\text{C}_{12}\text{H}_{13}\text{S}_4$, then, we must ascribe the faculty of replacing the three equivalents of hydrogen in the ammonia. But, in what manner the elements are grouped in this complex molecule, whether we have here to assume a very unstable tribasic radical, or whether special molecules are inserted for each of the hydrogen equivalents in the ammonia,—must be left for further experiments to decide, and I think it desirable to postpone for the present any speculation on the subject.

The preceding experiments have led me to some observations no longer connected with the original problem of the inquiry, which appear, however, of sufficient interest to be mentioned.

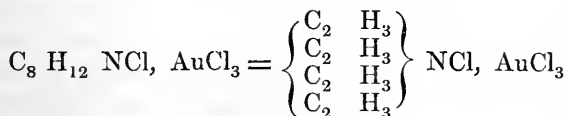
Liebig and Woehler in their memoir on Thialdine state, that the whole of the nitrogen of this base is eliminated in the form of ammonia, when the compound is decomposed by nitrate of silver. This deportment appeared to furnish an easy mode of controlling the formula of methyl-thialdine. After the decomposition of this body by nitrate of silver, I expected to find the whole of the nitrogen in the residuary liquid in the form of methylamine. On performing the experiment, it was found that the liquid contained considerable quantities of ammonia, but together with the latter alkali a fixed base. This unexpected deportment reminded me of some experiments on the action of oxide of silver on thialdine, which were published several years ago,* and from which their author had inferred that thialdine was capable of being converted into *leucine*. Were the phenomena observed by myself of an analogous character? Had the experiment above mentioned given rise to the formation of methylated *leucine*?

* Annalen der Chem., xc, 184.

The experiment was therefore repeated with a larger quantity of substance and the iodide of methyl-thialdine treated with freshly precipitated oxide of silver instead of nitrate of silver. To avoid as far as possible, secondary decompositions, the reaction was accomplished at the common temperature, and only completed in the water bath. The phenomena remained the same,—separation of iodide of silver and a copious evolution of aldehyde, which gave rise to the formation of a mirror of metallic silver. The liquid filtered off from the precipitate contained a considerable quantity of silver, and evolved, on the addition of hydrochloric acid for the removal of the silver, a very perceptible odour of acetic acid. The solution freed from silver, furnished upon evaporation a saline mixture, in which sal-ammoniac could be detected without difficulty. But in this case, also, a fixed base was found to be associated with the ammonia. The deportment of this solution with bichloride of platinum left no doubt in this respect. On a former occasion, I pointed out that in determining the equivalent of an organic base, the bichloride of platinum may be conveniently replaced by terchloride of gold which has since been very frequently used for this purpose. This reagent is of particular advantage if it be necessary to eliminate an alkaloid from a solution containing ammonia, the double compound of terchloride of gold and chloride of ammonium being very soluble in water, and was, therefore, specially applicable in the present case. On adding terchloride of gold to the saline mixture under examination, a fine yellow crystalline precipitate was immediately thrown down, all the ammonia remaining in solution. The gold-precipitate could be recrystallized from boiling water without decomposition; its analysis furnished the following results :

I. 0.6685 grm. of the salt, dried at 100°, when burnt with chromate of lead, gave 0.2765 grm. of carbonic acid, and 0.179 grm. of water.

II. 0.265 grm. of salt left on ignition 0.1235 grm. of gold. These numbers lead to the formula :



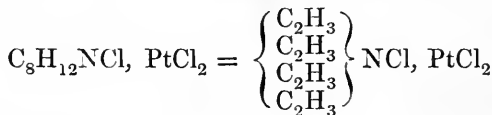
which represents the double compound of chloride of tetramethyl-ammonium and terchloride of gold.

| | Theory. | | Experiment. | |
|-------------------------|---------|--------|-------------|-------|
| | | | I. | II. |
| 8 eq. of Carbon | 48 | 11.62 | 11.28 | — |
| 12 eq. of Hydrogen .. | 12 | 2.91 | 2.98 | — |
| 1 eq. of Nitrogen .. | 14 | 3.39 | — | — |
| 4 eq. of Chlorine .. | 142 | 34.38 | — | — |
| 1 eq. of Gold | 197 | 47.70 | — | 47.36 |
| <hr/> | | | | |
| 1 eq. of Gold-salt | 413 | 100.00 | | |

In order to verify the formation of a tetramethyl-ammonium-compound, some further experiments were made. The solution of iodide of methyl-thialdine, desulphurised by oxide of silver, was submitted to a protracted distillation, when a considerable quantity of an alkaline liquid was obtained, which proved to consist of *ammonia*.* The alkaline residuary liquid in the retort, after considerable concentration, deposited a crystalline silver-salt which possessed all the properties of *acetate of silver*. The solution filtered off from this salt, freed from dissolved silver by addition of hydrochloric acid, (when the presence of acetic acid became again perceptible,) furnished, on evaporation, a saline mixture, which obviously contained much less ammonia than the liquid used in the preparation of the gold-salt. The solution of the saline mixture gave with bichloride of platinum a crystalline precipitate, which was recrystallized from boiling water. The first crystals deposited on cooling were magnificent perfectly formed octohedrons, which I easily recognised as the platinum-compound of tetramethyl-ammonium. Analysis furnished the following results:

0.5335 grm. left on ignition 0.188 grm. = 35.24 p. c. of platinum.

The formula



requires 35.35 p. c. of platinum.

* The basic distillate was saturated with hydrochloric acid and converted into a platinum-salt; by the analysis of this salt the ammonia was identified.

I.—0.1865 grm. of platinum-salt gave 0.081 grm. = 43.8 p. c. of platinum.

II.—0.307 grm. of platinum-salt gave 0.134 grm. = 43.6 p. c. of platinum.

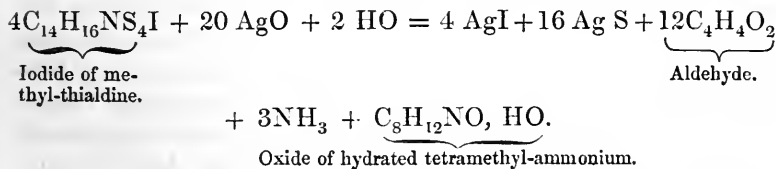
The ammonium-compound contains 44.22 p. c. of platinum.

The mother-liquor of the salt furnished, after considerable evaporation, a second crystallisation likewise in octohedrons. Experiment, however, showed these crystals to consist nearly entirely of ammonio-chloride of platinum.

0.257 grm. of salt gave 0.110 grm. = 42.8 p. c. of platinum.

These experiments prove that the nitrogen of iodide of methyl-thialdine, on treating this substance with silver-compounds, is eliminated in the form, partly of ammonia and partly of oxide of tetramethyl-ammonium, aldehyde being simultaneously liberated, part of which, if oxide of silver be used, is converted into acetic acid. The decomposition may be readily expressed in an equation, although, in consequence of the formation of so highly methylated a compound, a rather large number of equivalents must be assumed as concerned in the reaction; 4 eq. of iodide of methyl-thialdine, 20 eq. of oxide of silver, and 2 eq. of water, contain the elements of 4 eq. of iodide of silver, 16 eq. of sulphide of silver, 12 eq. of aldehyde, 3 eq. of ammonia, and 1 eq. of hydrated oxide of tetramethyl-ammonium.

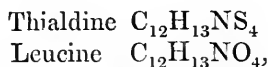
The following equation represents this change :



The acetic acid is a further product of the oxidation of the aldehyde.

The absence of any leucine-like compound among the products of decomposition of iodide of methyl-thialdine induced me to repeat the experiment on the action of oxide of silver upon thialdine itself.

The transformation of thialdine into leucine announced several years ago, and apparently very intelligible by the analogy of the formulæ of the two bodies :



has not failed to rivet the attention of chemists. The artificial

construction of organic bodies, the formation of complex substances by the aid of simpler compounds, has been attempted of late with predilection, and science is already in possession of several most interesting instances of this kind. But the passage of an acetyl-compound into a member of the amyl-series—for such leucine must be considered—leaping over all the intermediate terms, is a fact to which there are but few parallel cases at the present moment.

The extraordinary character of this reaction, together with the non-appearance of any further information regarding this mode of forming *leucine*, has already created doubts in the minds of chemists, whether the observed substance was actually leucine. But as yet nobody appears to have taken the trouble to clear up these doubts experimentally.

My experiments, which in conclusion I may briefly mention, have led me to the conviction that the statement regarding the convertibility of thialdine into leucine must have been caused by an error of observation.

In the first place, I have established that the nitrogen of thialdine, when this body is decomposed by *nitrate of silver*, actually separates in the form of ammonia. The solution freed from silver and mixed with bichloride of platinum, furnished nothing but ammonio-chloride of platinum,* exactly as indicated by Liebig and Woehler. When submitted to the action of *oxide of silver*, thialdine, as might have been expected, exhibits exactly the same deportment. The liquid filtered off from the sulphide of silver deposited, on evaporation, lustrous crystalline plates which, both by their external appearance and by their analysis,† were readily identified as acetate of silver. The formation of acetic acid in a concentrated solution of aldehyde by the action of a substance which loses its oxygen as readily as oxide of silver, is easily intelligible.

The mother-liquor, when further evaporated, yielded a second crystallisation, in which the physical characters of acetate of silver were somewhat masked by the presence in the solution of an uncrystallisable substance (aldehyde-resin) which adhered even after a second crystallisation. Analysis, however, proved these crystals

* 0.3215 grm. of platinum-salt gave

0.1405 grm. = 43.7 p. c. of platinum.

† 0.225 grm. of silver-salt left on incineration 0.146 grm. = 64.88 p. c. of silver.

—Acetate of silver contains 64.67 p. c. of silver.

likewise to be acetate of silver.* The mother-liquor contained, together with acetate of silver, acetate of ammonium and small quantities of a non-crystalline body.

Since leucine is a well-characterized and very stable body, I was inclined to attribute my want of success to my own unskilfulness rather than to the error of another observer. The operation was therefore repeated several times, and always with the same result; but I could not make up my mind to deny the formation of leucine from thialdine until experiment had refuted every other mode of explanation.

For this purpose, it was not sufficient to prove that, in the decomposition of thialdine by oxide of silver, ammonia is eliminated; it was necessary to prove that the total amount of nitrogen is converted into ammonia.

2.065 grm. of thialdine were desulphurised by means of oxide of silver, in the presence of water at the common temperature, and the liquid freed from silver, by hydrochloric acid, was mixed with bichloride of platinum and evaporated to dryness. The ammonio-chloride of platinum formed, when washed with ether-alcohol, weighed 2.792 grm.; according to theory 2.828 grm. should have been obtained.

In a second experiment, 0.317 grm. of thialdine sealed into a glass tube with water and an excess of oxide of silver, and exposed to the temperature of boiling water for four hours, furnished, when treated in the same manner as in the previous experiment, 0.430 grm. of ammonio-chloride of platinum. According to theory, 0.436 grm. should have been obtained.

These experiments leave no doubt.

Whilst occupied with this subject, the "Annalen" brought the news of the interesting transformation of leucine into amylamine. This deportment of leucine induced me to perform in addition the following experiment: several grammes of thialdine were desulphurised, the hydrochloric solution evaporated to dryness, and submitted to distillation with hydrate of lime. In the alkaline distillate, I was unable to discover a trace of amylamine, although this substance is well known to me. The platinum-salt prepared from the alkaline distillate, by evaporation to dryness with bichloride of platinum, was found to be pure ammonio-chloride of platinum.

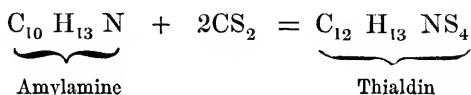
* 0.327 grm. silver-salt left on ignition 0.2105 grm. = 64.37 p. c. of silver.

0.661 grm. of platinum-salt left on ignition

0.2909 grm. = 44.019 p. c. of platinum.

Hence thialdine, when treated with oxide of silver, as might have been expected, undergoes the same decomposition which Liebig and Woehler had effected by nitrate of silver. It furnishes in this process, aldehyde, acetic acid, and ammonia, but *no Leucine*.

In conclusion, a remark which refers to a question connected with this alleged formation of leucine. Soon after the statement regarding this subject had been made, Wagner* observed that the action of bisulphide of carbon upon amylamine gives rise to the formation of a crystalline compound. This compound was not analyzed, but Wagner suggested that possibly it might be thialdine:



and that, in case this assumption proved to be correct, the reaction of bisulphide of carbon upon the homologues of ammonia might lead to the artificial formation not only of leucine, but of glycocine alanine, etc. A close connection between these substances and the alcohol bases has indeed been established, by the recent observation to which I have just alluded.

During my experiments on the deportment of bisulphide of carbon with organic bases, I have also had occasion to study the compound of amylamine with bisulphide of carbon. It is only necessary to compare superficially this substance with thialdine, in order to perceive at once that they are two absolutely different compounds; and if there be still a chance of producing leucine from amylamine, it is not likely that so desirable a result will be accomplished by the intervention of thialdine.

* Journal für Practische Chemie, lxi, 350.

II.—*Miscellaneous Observations.*

By A. W. HOFMANN.

I.—ON NITROPHENOL.

By experiments which I communicated to the Chemical Society* several years ago, on the action of nitrous acid upon several alkaloids, it was shown that ethylamine and amylamine are readily converted under these conditions into nitrite of ethyl and of amyl. It can scarcely be doubted that these compounds are secondary products of decomposition, and that the first stage of the reaction consists in the formation of ethylic and amylic alcohols, which, by the further action of the nitrous acid, are converted into nitrites. Appropriately modified experiments will probably show that the reaction may be arrested in its first phase, and then the alcohols will actually be separated. This result was in fact obtained in the corresponding experiment with aniline. I found that careful management certainly converts this base into phenol or phenyl-alcohol, a transformation which had been previously observed by Hunt. My experiments proved, however, that aniline likewise yields with predilection the nitro-alcohol. In the short note referred to, I briefly mentioned the discovery of the nitrophenylic alcohol, hoping that I might be enabled to give a more perfect account of this beautiful compound at a later period. It was not until during the last year that I found leisure to return to this subject, when I learnt from Professor Fritzsche of St. Petersburg, that he wished to take up the examination of nitrophenol. I have, therefore discontinued this inquiry, and intend here to communicate only some observations mostly made years ago which establish the nature of nitrophenol.

On passing nitrous acid into aniline, or binoxide of nitrogen into nitrate of aniline, a brown resinous mass is formed, exhibiting traces of crystalline structure. If this product be distilled with water, light yellow oily drops pass over with the water, which generally solidify into spherical aggregates of needles in the condenser.

The same compound is formed by distilling aniline with dilute nitric acid, although only in minute quantities, the larger portion

* Quarterly Journal, vol. iii, p. 231.

of the base being converted into dinitrophenol (nitrophenesic acid) and trinitrophenol (nitrophenisic acid) which may be readily recognised by their properties, especially by the formation of the characteristic ammonium- and potassium-compounds.

An analysis which I shall give hereafter, having sufficiently established the nature of the new body, its preparation from phenol naturally suggested itself. There is in fact no difficulty in procuring this substance from phenylic alcohol; but this process yields but a comparatively small amount, dinitrophenol and trinitrophenol being always obtained in predominant quantities.

Two different methods may be adopted for preparing nitrophenol from phenol. Small quantities of phenol, well cooled by a frigorific mixture, are added to small portions of the strongest nitric acid, likewise well cooled; the mixture thus obtained is immediately poured into water. The experiment is best performed in test tubes. It is necessary carefully to avoid every continued reaction which would unavoidably produce higher nitro-compounds. By distilling the mixture of water, oil, and resin, the nitrophenol is easily purified.

The second method consists in mixing the phenol with a sufficient quantity of water to produce a homogeneous liquid. This mixture is then distilled with an equal volume of ordinary nitric acid. In the commencement of the operation, nothing but water passes over; suddenly, however, a reaction takes place, the liquid in the retort becoming brown, a resinous mass separates, and on continuing the distillation, oily drops of nitrophenol pass over with the vapour of water. The former method frequently fails, but yields when successful a larger product than the latter. By this last-mentioned process, nitrophenol is always obtained; but many operations are required in order to procure a moderate quantity of this substance. On the whole I am inclined to give the preference to the second process.

Nitrophenol, whether prepared from aniline, or procured by one or the other process from phenol, forms a beautiful light yellow crystalline mass of an aromatic and rather agreeable odour. It fuses at 42° , forming a transparent, almost colourless oil, which resolidifies at 26° . The boiling point of nitrophenol is 216° .

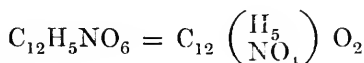
The analysis of this substance furnished the following results. Analysis I. refers to a less pure product obtained from aniline.

Analysis II. was made with a perfectly pure compound prepared from phenol.

I. 0.199 grm. of substance gave
 0.370 „ of carbonic acid and
 0.071 „ „ water.

II. 0.344 grm. of substance gave
 0.650 „ „ carbonic acid and
 0.115 „ „ water.

The formula



requires the following values.

| | Theory. | | Experiment. | |
|----------------------|---------|--------|-------------|-------|
| | | | I. | II. |
| 12 eq. of Carbon | 72 | 51.79 | 50.75 | 51.45 |
| 5 „ „ Hydrogen | 5 | 3.59 | 4.00 | 3.72 |
| 1 „ „ Nitrogen | 14 | — | — | — |
| 6 „ „ Oxygen | 48 | — | — | — |
| <hr/> | | | | |
| 1 eq. of Nitrophenol | 139 | 100.00 | | |

The discovery of nitrophenol fills a gap in the series of the nitro-derivatives of phenol, which is thus completed.

Phenol . . . $C_{12} \quad H_6 \quad O_2$ Phenylic alcohol.
 Nitrophenol $C_{12} \left(\begin{smallmatrix} H_5 \\ NO_4 \end{smallmatrix} \right) O_2$ Nitrophenasic acid.
 Dinitrophenol $C_{12} \left(\begin{smallmatrix} H_4 \\ (NO_4)_2 \end{smallmatrix} \right) O_2$ Nitrophenesic acid.
 Trinitrophenol $C_{12} \left(\begin{smallmatrix} H_3 \\ (NO_4)_3 \end{smallmatrix} \right) O_2$ Nitrophenisic acid.

Nitrophenol is but slightly soluble in water, to which it imparts a distinctly acid reaction. It is extremely soluble in alcohol and ether. The alcoholic solution is strongly acid. From the alcoholic as well as from the ethereal solution, the compound is obtained in magnificent crystals on slow evaporation.

On pouring potassa, soda, or ammonia on nitrophenol, the substance is at once converted into crystalline compounds of a magnificent scarlet colour. These are salts of nitrophenol, which,

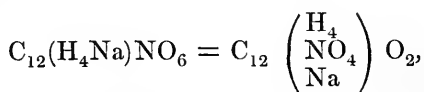
accordingly, may also be called nitrophenazic acid. The colour of these salts is so characteristic, that in preparing nitrophenol, the alkalis may be conveniently employed as reagents for the compound. When the addition of potassa or ammonia to the product of the reaction furnishes yellow crystals, or yellow solutions, it may be inferred with certainty that the reaction has gone too far, and that dinitrophenol and trinitrophenol only have been produced.

The alkaline salts of nitrophenol, which are difficultly soluble or insoluble in an excess of the alkalis, dissolve with the greatest facility in pure water. It is consequently rather difficult to purify them by crystallisation. A tolerably pure sodium-compound was obtained by treating the acid with an excess of caustic soda, allowing the compound to remain in contact with the air until the whole of the uncombined soda had been carbonated, and by recrystallising it from absolute alcohol.

0.515 grm. of the salt gave, on being treated with hydrochloric acid

0.1898 grm. of chloride of sodium = 14.48 p. c. of sodium.

The formula



requires 14.28 p. c. of sodium.

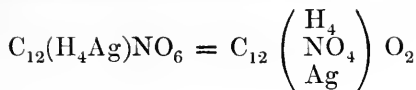
The solution of the sodium-compound yields no precipitate with chloride of barium and calcium. Acetate of lead and protochloride of mercury throw down orange-red compounds. Nitrate of silver furnishes a deep orange-red precipitate, which is difficult to wash free from the soluble salt, on account of its gelatinous character, and also because it is rather soluble in water.

On analysis the following numbers were obtained :

I. 0.2365 grm. of the silver-salt gave, on ignition
0.1030 „ = 43.5 p. c. of silver.

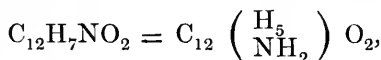
II. 0.549 grm. silver-salt gave
0.3235 „ of chloride of silver = 44.33 p. c. of silver.

The formula

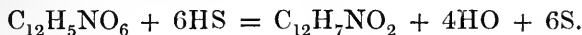


requires 43.92 p. c. of silver.

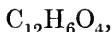
The idea of submitting nitrophenol to the action of reducing agents naturally suggested itself. The ammoniacal solution of the compound is but difficultly and slowly obtained. The reduction succeeded, however, rapidly and without difficulty in a potassa- or soda- solution. There is formed in the reaction, together with a deposit of sulphur, a compound perfectly different from nitrophenol, which crystallises in white needles, soluble in water, alcohol, and ether, and possessing, like the amidated aromatic acid, at once feebly acid and feebly basic properties. This substance, to which the name amido-phenol might be given, obviously contains



and is formed according to the equation



Amido-phenol is a rather unstable compound. In contact with the air, it is rapidly blackened, especially when in solution. From reasons to which I have already alluded, I have not prosecuted any further the study of this compound, which promises many interesting results. The action of nitrous acid upon amido-phenol will probably yield the acid,



which is but little known at present, and whose alleged chlorine- and nitro- substitutes—chloroniceic and nitrochloroniceic acid, chloronicein, &c.—attracted, some years ago, the lively, but it would appear, undeserved attention of chemists.

II.—ON A NEW MODE OF FORMING TRIETHYLAMINE.

RESEARCHES on the constitution of the nitrogenous organic basis, which I zealously prosecuted some years ago, and the results of which were communicated to the Chemical Society, have been, by circumstances, interrupted for some time. Nearly all the observations recorded in my communications refer to the primary or amidogen-bases, *i. e.*, the compound ammonias in which one equivalent of hydrogen is replaced by an organic molecule. Of the secondary and tertiary bases (imidogen- and nitrile-bases) *i. e.*, the ammonias in which two or three equivalents of hydrogen are replaced, and of the fixed ammonium-bases, little more is known at present than their mode of formation and their composition.

On again taking up this subject, lately, it appeared of paramount importance to search for new and, if possible, simpler methods of forming the secondary and tertiary bases.

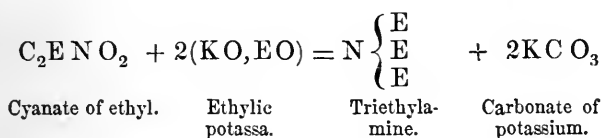
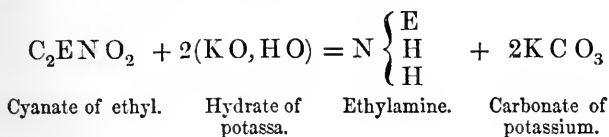
Of the several experiments made for this purpose, on which I intend to report at another opportunity, I may be allowed even now to quote a result which appears to be capable of a more general application.

One of the common methods of preparing the amidogen-bases, consists in treating the cyanic ethers with hydrate of potassa, as observed by Wurtz. To take a special case, cyanate of ethyl, when treated with hydrate of potassa, assimilates two equivalents of water, and splits into ethylamine which is set free, and carbonic acid which is fixed by the alkali. An appropriate modification of this reaction appeared to afford a means of passing directly from cyanate of ethyl to *triethylamine*. For this purpose it was only necessary to offer to the cyanate of ethyl two equivalents of oxide of ethyl, instead of two equivalents of water. The action of cyanate of ethyl upon ethylic potassa, appeared to involve the conditions necessary for accomplishing this result.

Experiment has fully confirmed this anticipation.

On digesting for several hours, at a moderate temperature, a mixture of cyanate of ethyl with pure ethylic potassa or soda (*i. e.*, absolute alcohol, saturated as far as possible with potassium or sodium), and distilling subsequently upon a sand-bath, a strongly alkaline liquid, containing alcohol, is obtained. Saturated with hydrochloric acid, this liquid furnishes, on evaporation to dryness, a residue from which a considerable quantity of triethylamine is expelled, upon addition of potassa.

The analogy of the two processes, for the formation of ethylamine and triethylamine is obvious, on glancing at the following equations :



There could be no doubt regarding the identity of the alkaline compound thus formed with triethylamine. The base floating on the surface of the saturated aqueous solution possessed, in a marked manner, the characteristic odour of triethylamine. In order to exclude the possibility of a mistake, the hydrochloric solution of the compound was mixed with a solution of bichloride of platinum. Only after protracted standing of the highly concentrated solution, deep orange-coloured well-formed crystals of platinum-salt were deposited, the physical characters of which were still fresh in my memory.

The determination of platinum furnished the following results :

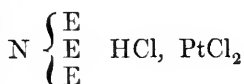
First crystallisation :

I. 0.3055 grm. salt gave 0.100 grm. platinum.

Second crystallisation :

II. 0.31025 grm. salt gave 0.101 grm. platinum.

The percentages of platinum corresponding to these numbers agree with the formula.



| Theory. | Experiment. | |
|----------------|-------------|-------|
| | I. | II. |
| Platinum 32.12 | 32.73 | 32.55 |
| | | P |

The small excess of platinum, which must be obviously attributed to a minute admixture of ethylamine, cannot be a matter of surprise, if we recollect that the smallest trace of moisture, either in the ethylic potassa or in the cyanate of ethyl, must lead to the formation of a corresponding quantity of ethylamine.

I have already applied this reaction in various directions, and shall communicate the results which I have obtained, at a future period. On considering how frequently, in the action of hydrated potassa upon organic substances, the hydrogen of the water of hydration is assimilated by the product of decomposition, the substitution of ethylic potassa for the hydrate appears in many cases to promise a new means of ethylation. The facility, however, with which ethylic potassa decomposes, even at comparatively low temperatures, must always be an obstacle to an extensive use of this reaction.

III.—FORMATION OF THE CRYSTALLINE COMPOUND OF HYDRIODIC ACID AND PHOSPHORETTED HYDROGEN.

THIS beautiful body, which, in consequence of the recent inquiries into the nature of the phosphorus-bases, has acquired new and additional interest, is not very easily produced. Often it is obtained in well-defined crystals, as an accidental by-product in the last stage of the preparation of anhydrous hydriodic acid, whilst distillation of phosphorus, water, and iodine, carried out specially with the view of producing it, frequently furnishes either no result at all, or only a scanty crop of impure crystals, however carefully the given prescription may have been followed. This is particularly undesirable if the operation be performed as a lecture-experiment, not to speak of the facility with which phosphorus is carried over, or of the danger of explosion. I have lately observed the formation of the body in question, under circumstances which exclude this inconvenience, and which may, therefore, be recommended as an illustration for lectures.

Iodine, gently heated in dry phosphoretted hydrogen, decomposes this gas: iodide of phosphorus and hydriodic acid are

generated, and the latter combines with the excess of phosphoretted hydrogen.



The delivery-tube which supplies the non-spontaneously inflammable phosphoretted hydrogen, is connected with a drying tube containing lime, which in its turn passes into a long combustion-tube, fixed horizontally. In the front part of this tube are placed a few crystals of iodine. As soon as the dry phosphoretted hydrogen gas reaches the crystals, they begin to change colour, and when gently heated with a spirit-lamp, are rapidly converted into scarlet iodide of phosphorus; whilst, at the same time, the cold part of the tube becomes coated with a silver-like crystalline network of hydriodate of phosphoretted hydrogen.

The experiment was frequently repeated without an explosion occurring.

I have endeavoured, but without success, to produce analogous compounds, by heating iodine in antimonetted and in arsenetted hydrogen.

XIX.—On the Action of Sulphuric Acid on Anisic Acid.

BY LOUIS ZERVAS.

IN their paper on the action of sulphuric acid on the Amides and Nitriles, Dr. Hofmann and Mr. Buckton have directed the attention of chemists to the more general occurrence of disulpho-acids, and established the formation of such acids in several series of compounds.

At the suggestion of Dr. Hofmann, I have, in his laboratory, endeavoured to obtain the disulpho-acids of different bodies, which hitherto had not been examined in this direction.

The experiments to be described in the following pages, refer particularly to the aromatic acids with six equivalents of oxygen. I have chosen, in the first place, one of the most characteristic representatives of this class, *anisic acid*.

The decomposition of acetic acid, under the influence of the alkalis, into marsh gas and carbonic acid, and its conversion by

the action of sulphuric acid into a substance which may be considered as a compound of marsh gas with 4 eq. of anhydrous sulphuric acid, left scarcely a doubt as to the deportment of the acid under examination with sulphuric acid. Anisic acid, by the action of the alkalis, splits into carbonic acid and anisol; the formation of a *di-sulphanisolic acid* was therefore exceedingly probable. Experiment has corroborated this anticipation.

Preparation of Anisic Acid.—A comparatively small quantity of pure anisic acid is obtained by treating oil of aniseed in the usual way with nitric acid, since the formation of a considerable quantity of nitroanisic acid can scarcely be prevented.

It appeared, therefore, highly desirable to find out a new mode of preparation. By treating oil of aniseed with bichromate of potassium and sulphuric acid, a much better result is obtained.

Six parts of bichromate of potassium are dissolved in a capacious vessel in 9 parts of water and 7 parts of concentrated sulphuric acid. To this solution, 1 part of oil of aniseed is then added, and the whole agitated. After a few minutes, a violent reaction sets in, the liquid intumesces powerfully, and is apt to run over unless the vessel be rather large. After the lapse of half an hour, cold water is added in order to separate the anisic acid, which is very little soluble in this menstruum. By crystallisation from hot alcohol, the acid may be obtained in a state of purity.

The quantity of acid procured by this process averages about 50 per cent. of the oil employed.

Action of fuming Sulphuric Acid on Anisic Acid at the Temperature of 100° C.—If anisic acid be mixed with Nordhausen sulphuric acid, so as to form a syrupy mass, and the mixture be digested on the water-bath for about two hours, the liquid may then be diluted with water without becoming turbid. A smaller or larger quantity of anisic acid is invariably precipitated if the digestion has not been continued long enough. On adding an excess of well-washed carbonate of lead to this solution, in order to remove the free sulphuric acid, and filtering the hot solution obtained by repeatedly boiling out the lead-precipitate, a considerable quantity of brilliant crystalline needles are deposited on cooling. The mother liquor furnishes on evaporation a further crop. These needles are the lead-salt of a sulpho-acid, which I propose to call *sulphanisic acid*.

Sulphanisate of lead.—This salt is little soluble in cold water, not at all soluble in alcohol; it dissolves, however, easily in boiling water, and may be purified by recrystallisation from hot water.

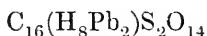
The salt becomes less soluble by being repeatedly recrystallised. The analysis of the salt, dried at 100° C, gave the following results.

- I. 0·5258 grm. gave 0·351 grm. of sulphate of lead.
 II. 1·2703 grm. „ 0·8421 grm. „ „
 III. 0·3939 grm. fused with chlorate of potassium and carbonate of sodium, gave 0·2024 grm. sulphate of barium.
 IV. 0·7052 grm. burnt with oxide of copper gave 0·5408 grm. of carbonic acid, and 0·1137 of water.
 V. 0·8248 grm. gave 0·6307 grm. of carbonic acid, and 0·1322 grm. water.
 VI. 2·0220 grm. dried at 175° C lost 0·0772 grm. of water.

Percentages corresponding to these numbers :

| | I. | II. | III. | IV. | V. |
|----------|-------|------|------|-------|-------|
| Lead | 45·61 | 45·3 | — | — | — |
| Carbon | — | — | — | 20·92 | 20·85 |
| Hydrogen | — | — | — | 1·79 | 1·78 |
| Sulphur | — | — | 7·05 | — | — |

leading to the formula



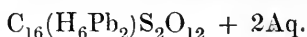
as may be seen by the following comparison—

| | | Theory. | | Experiment. | |
|----------|----|---------|--------|-------------|-------|
| Carbon | .. | 16 | 96 | 21·09 | 20·89 |
| Hydrogen | .. | 8 | 8 | 1·76 | 1·79 |
| Lead | .. | 2 | 207·14 | 45·51 | 45·45 |
| Sulphur | .. | 2 | 32 | 7·03 | 7·05 |
| Oxygen | .. | 14 | 112 | 24·61 | — |
| | | <hr/> | | <hr/> | |
| | | 455·14 | | 100·00 | |

The determination of water in experiment VI. shows, however, that the salt contains two equivalents of water.

| | | Theory. | | Experiment. | |
|----------------------------|---|---------|-------|-------------|---|
| 1 eq. of the dry lead-salt | . | 437·14 | 96·05 | — | — |
| 2 eq. of water | . | 18 | 3·95 | 3·81 | — |
| | | <hr/> | | <hr/> | |
| | | 455·14 | | 100·00 | |

and the proper formula of the salt is therefore



Sulphanisate of lead may also be obtained by treating anisic acid with the ordinary hydrate of sulphuric acid at a temperature of 110°C .

Sulphanisic Acid.—By decomposing the lead-salt in the usual way, by means of hydrosulphuric acid, free sulphanisic acid is readily obtained. It may be boiled without decomposing, and furnishes, when slowly evaporated, small crystals. They are insoluble in alcohol, but soluble in ether. After having been dried in the water-bath, sulphanisic acid may be heated as high as 170° without fusing or suffering decomposition. 0.8926 gm. dried over sulphuric acid, when heated to 100°C ., lost 0.0612 gm. water, corresponding to 6.9 per cent.

I. 0.3801 gm. (dried at 100°C .) fused with chlorate of potassium and carbonate of sodium gave 0.3915 gm. of sulphate of barium.

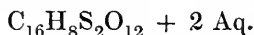
II. 0.2142 gm. gave 0.2202 gm. of sulphate of barium.

These sulphur-determinations lead to the formula



| | Theory. | Experiment. |
|-------------|---------|-------------|
| Sulphur . . | 13.8 | 14.13 14.10 |

The acid dried over sulphuric acid has the formula



| | Theory. | Experiment. |
|------------------|-----------|-------------|
| 1 eq. of acid . | 232 92.8 | — |
| 2 eq. of water . | 18 7.2 | 6.9 |
| | <hr/> 250 | <hr/> 100.0 |

Sulphanisate of Barium.—Beautiful readily soluble crystals obtained by saturating the acid by carbonate of barium.

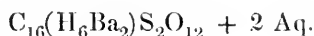
The analysis of the salt dried at 100° furnished the following results:—

I. 0.4596 gm. gave 0.2783 of sulphate of barium.

II. 0.8496 gm. „ 0.5140 „ „

III. When heated from 100° to 170° it lost 4·7 per cent. of water.

The formula



requires the following values:—

| | | | | Experiment. | | |
|----------|---------|-------|-------|-------------|------|------|
| Theory. | | | | I. | II. | III. |
| Carbon | . . 16 | 96 | 24·92 | — | — | — |
| Hydrogen | . . 6 | 6 | 1·56 | — | — | — |
| Barium | . . 2 | 137·2 | 35·62 | 35·73 | 35·7 | — |
| Sulphur | . . 2 | 32 | 8·31 | — | — | — |
| Oxygen | . . 12 | 96 | 24·92 | — | — | — |
| Water | . . . 2 | 18 | 4·67 | — | — | 4·7 |
| <hr/> | | | | | | |
| 385·2 | | | | 100·00 | | |

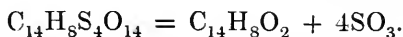
The potassium- and sodium-salts of sulphanisic acid crystallise easily; both are, however, surpassed in beauty by the ammonium-salt, which forms very long and fine needles.

The silver-salt is obtained by treating the acid with carbonate of silver; it is rather difficultly soluble in water, and crystallises in scales.

Action of Nordhausen Sulphuric Acid upon Anisic acid at a higher temperature. — If a mixture of the two acids be heated to 140° instead of digesting it on the water-bath, a gas is generated which is easily recognised as carbonic acid. The evolution of carbonic acid is gradually increased, until the temperature has reached 200°. On raising the heat still further, an evolution of sulphurous acid is distinctly perceptible, and the operation must be interrupted in order to prevent further alterations.

In order to examine the product furnished by sulphuric acid under these altered circumstances, a portion of the syrupy liquid was saturated with carbonate of barium and the solution separated from the sulphate of barium evaporated; but, by this means only very impure crystals were deposited. In order to obtain a purer compound, the sulphuric acid solution was saturated with carbonate of lead, the filtrate from the lead-salt evaporated to dryness, and the residue dissolved in as little water as possible.

Addition of strong alcohol to this solution threw down a considerable precipitate, which was washed with alcohol and decomposed by means of sulphuretted hydrogen. The acid thus separated, when saturated with carbonate of barium, gave small crystalline grains, which became colourless by repeated recrystallisation. If we remember the transformation of anisic acid by the action of alkalis, into carbonic acid and anisol, if we consider moreover the circumstances under which the new acid is formed, we cannot possibly have any doubt as to its composition. This new acid, which may be called *Disulphanisolic* acid, must obviously contain

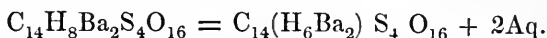


Experiment has fully corroborated this view, as is evident from the following analysis of the barium-salt :

- I. 0.4170 grm. of barium-salt gave 0.2319 grm. of sulphate of barium.
- II. 0.8864 grm. gave 0.493 of sulphate of barium.
- III. 0.5412 grm. oxidised by means of chlorate of potassium, gave 0.5943 grm. sulphate of barium.
- IV. 0.4069 grm. burnt with oxide of copper and chromate of lead, gave 0.2617 grm. of carbonic acid and 0.0699 grm. of water.

| Percentages : | I. | II. | III. | IV. |
|---------------|-------|------|-------|-------|
| Carbon | — | — | — | 19.13 |
| Hydrogen | — | — | — | 1.93 |
| Barium | 32.72 | 33.0 | — | — |
| Sulphur | — | — | 15.07 | — |

These numbers lead to the formula



which requires the following values.

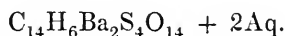
| | | Theory. | | Experiment. |
|----------|-------|---------|--------|-------------|
| Carbon | .. 14 | 84 | 19.94 | 19.13 |
| Hydrogen | .. 8 | 8 | 1.89 | 1.93 |
| Barium | .. 2 | 137.2 | 32.6 | 32.86 |
| Sulphur | .. 4 | 64 | 15.19 | 15.07 |
| Oxygen | .. 16 | 128 | 30.48 | |
| | | <hr/> | <hr/> | |
| | | 421.2 | 100.00 | |

It appeared of some interest to ascertain whether the new acid might also be prepared directly from anisol. A quantity of this substance was therefore heated together with fuming sulphuric acid, and a salt obtained by saturating with carbonate of barium, which crystallised exactly like the disulphanisolate of barium. Dried at 100° , and subjected to analysis, it gave the following results :

- I. 0.5436 grm. gave 0.3017 grm. of sulphate of barium.
 II. 0.3517 grm. „ 0.1959 grm. „ „ „
 III. 1.3889 grm. lost 0.0605 grm. water when heated to 175°C

No sulphur-determination was made, but it was ascertained that the hydrochloric solution of the salt fused with chlorate of potassium and carbonate of sodium, still yielded a precipitate with chloride of barium, showing that the salt contains more sulphuric acid than corresponds to the barium. From the analysis, it is obvious that the barium-salt prepared from anisol is identical with the barium-salt obtained by means of anisic acid.

The formula



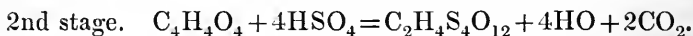
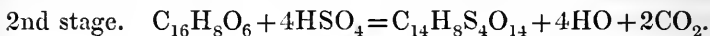
requires the following values, which I place in juxta-position with the experimental percentages.

| Theory. | | Experiment. | | |
|---------|--------|-------------|-------|------|
| | | I. | II. | III. |
| Barium | . 32.6 | 32.7 | 33.28 | — |
| Water | . 4.3 | — | — | 4.35 |

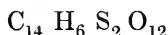
The difficulty of obtaining larger quantities of disulphanisolic acid has prevented me from following up the examination of this acid any further. I will only observe that the acid obtained by the decomposition of the lead-salt did not crystallise, and was decomposed on boiling.

POSTSCRIPT.

From the preceding experiments, it is obvious that the action of sulphuric acid upon organic acids with six equivalents of oxygen, is perfectly similar to that which this agent exerts upon acids with four equivalents of oxygen.

Acetic Acid.*Anisic Acid.*

There can be no doubt that salicylic acid, in many respects so closely allied to anisic acid, must exhibit a similar deportment. Mr. Baldwin Duppa has been occupied with this subject in my laboratory, and has already studied the first term, *sulpho-salicylic acid*,



which forms extremely beautiful compounds.

On submitting salicylic acid to the action of an excess of sulphuric acid, at a temperature of 180° , the same phenomena present themselves which are noticed in the case of anisic acid; a powerful evolution of carbonic acid ensues, and the solution now contains a new sulpho-acid. As yet Mr. Duppa has not succeeded in obtaining this acid in a state of sufficient purity for analysis, but it may be assumed, without much hesitation, that it will be found to be *disulphophenic acid*

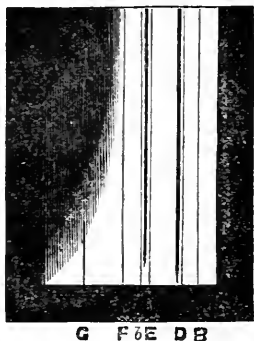


A. W. H.

XX.—*On an Optical Test for Didymium.*

BY J. H. GLADSTONE, Ph.D., F.R.S.

IN a recent paper on the use of the prism in qualitative analysis, I described a method by which the light transmitted through different thicknesses of a solution might be easily and satisfactorily determined. Among a number of solutions which I have since examined in that manner, was one of red nitrate of cerium. A prismatic appearance presented itself, in which the violet rays were seen to be gradually absorbed as they traversed greater thicknesses of the solution; but what attracted my attention more particularly, was two very black lines in the midst of what was otherwise a very luminous portion of the spectrum, the one in the yellow following directly upon the bright space immediately beyond the fixed line D, the other in the green, midway between E and *b*. The breadth of the first line was about one-thirtieth, and that of the other about one-fortieth of the whole breadth of the spectrum, the general appearance of which is represented in the annexed diagram.



From the extreme blackness of the first of these lines, even where the stratum of liquid was very thin, it seemed likely to prove a delicate test for whatever metal gave rise to it. But what was that metal? The specimen of nitrate was confessedly impure, and contained, in all probability, lanthanum and didymium as well as cerium. For the purpose of deciding between these different substances, Mr. Watts kindly lent me his specimens of pure compounds of cerium and didymium, namely, some of the brown oxide and pale pink sulphate of didymium, and of the fawn-coloured sesquioxide of cerium;* and I happened to have in my possession a small specimen of carbonate of lanthanum, given me by Mr. C. Greville Williams.

On examining by the prism the solutions of salts prepared from these, it was at once evident that the red nitrate of didymium produced the spectrum above described, while the pale rose-

* See his paper: Quart. Journ. Chem. Soc., vol. ii, p. 131.

coloured solutions of sulphate and chloride exhibited the two black lines without absorbing the violet, or otherwise affecting the normal spectrum.

The yellowish salts of peroxide of cerium, when dissolved, gradually cut off the violet and indigo rays, but did not produce the black lines. The colourless salts of the protoxide had no more effect on the transmitted light than pure water has.

The colourless solution of sulphate of lanthanum likewise absorbed no rays; but a faint dimness showed itself beyond D, when the stratum was thick, which, however, was attributed without hesitation to a trace of didymium.

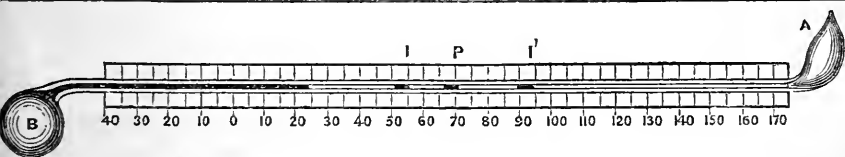
A prismatic examination of the light reflected from crystals of sulphate of didymium, also showed these lines, but the brown oxide did not exhibit them. So delicate, too, is this test, that one part of the sulphate dissolved in 1,000 parts of water showed the line in the yellow as a distinct darkening, when half an inch of the solution was looked through. I have no reason to think that other combinations of the metal would have less absorbent power; and as the atomic weight of the crystallised sulphate is 120, while that of didymium itself is 48, it may be fairly reckoned that 0.05 per cent. of didymium in a solution may be detected by this optical peculiarity. Nor does the presence of other bodies interfere with the application of this test; the alkalies and earths, and zinc, lead, and other metals which give colourless solutions, cannot affect it; and supposing iron, uranium, or other colorific metals to be present, it is immaterial, since they do not soon cut off the particular rays in which this absorption occurs. The only mineral compounds which, as far as I am aware, might practically interfere, are a salt of chromium or a permanganate; but the prism would at once reveal the presence of either of these; while, on the other hand, there is nothing, I believe, which could be mistaken for the peculiar bands of didymium. If it be desired to test a mineral or other body, for this metal, all that is necessary is to dissolve it in any acid, place the solution in the hollow glass wedge, and analyse by a prism the light of day, or of a gas-lamp, seen through a narrow slit. In this manner I have detected didymium not merely in cerite, but also (in minute quantity) in allanite—a mineral in which it seems to have been heretofore overlooked, although many analyses of this mineral have been published, and the presence of cerium as a constituent would lead to its being suspected.

In the analysis of rare earths, certain phenomena of colour have been sometimes suspected to arise from small quantities of a compound of didymium being mixed with them; but from the difficulty of establishing the presence or absence of this body, the question has not been resolved either affirmatively or negatively. No such doubt need any longer remain. As an instance, the faint yellowish colour frequently observed in yttria was suspected, by an eminent analyst, to be due to a trace of didymium. Now I happen to have a specimen of yttria made from ytthro-tantalite, and so coloured; but on subjecting it to prismatic examination, it showed no indication whatever of the black lines: the colour is doubtless due to Mosander's terbium.

The dilute solution of sulphate of didymium mentioned above, containing 1 part of salt to 1000 of water, appears quite colourless, and is, I think, the first instance of bands of absorption, beside Fraunhofer's lines, being detected in a colourless medium, though the possibility of such a case has been long recognised.

XXI.—*Notice of a new Maximum and Minimum Mercurial Thermometer.*

BY THE REV. JOHN G. MACVICAR, of Moffat.



A MERCURIAL minimum thermometer has long been a desideratum to the Meteorologist, as it is next to impossible to obtain a spirit thermometer which does not lag behind a mercurial one, so that, even with two instruments, he can seldom obtain the daily extremes with accuracy. Here both are given by one instrument, which is also available for the laboratory whenever it is desirable to note the extremes of temperature to which any substance under experiment has been exposed. The range of this instrument is 700° F, including all temperatures except the very lowest, and all heats to which organic substances can be subjected without decomposition.

A tube is taken with a fine cylindrical or rather regularly conical bore, such as thermometer tubing is generally obtained at the glass-works; a ball is blown as usual at that end where the bore is widest; and at the other end A, another ball is blown. Mercury is then introduced in proper quantity; and above the mercury a steel index, as in Rutherford's maximum thermometer. A very small globule of mercury is then introduced into the ball A, and the temperature of the instrument raised so that the mercury in the tube may be a sufficient number of degrees (say 40° for a thermometer to be used in giving the daily range of temperature) from the top of the tube. Let the tube be now held as represented in the figure, and on the cooling of the instrument the small globule of mercury in the expansion A, will descend into the tube, enclosing between it and the mercurial column of the bulb, a column of air about 40° long with a steel index in it. Now let another steel index be introduced above this mercurial piston, and when the instrument is all cool, let the bulb A be sealed as usual, and let fixed points be taken and a scale constructed.

The instrument being horizontal and the two indices brought by a small magnet one on each side of the mercurial piston, it is ready for use.

The piston will obviously travel up and down the tube as the top of the mercurial column issuing from the ball does, though alternately by the pressure of the air on either side of it.

The existing temperature is given by the upper surface of the mercurial piston; and by noticing whether it is convex or concave, it can be learned whether the temperature is at that moment rising or falling. In the figure it is 70° .

The maximum is obtained by observing the end of the upper index next the piston. In the figure it is 90° .

The minimum is similarly obtained from the index on the lower side, adding the number of degrees which the piston covers, as for instance in the figure 3° , giving 58° for the minimum represented.

After observation, both indices may be brought to their places, by the magnet, without moving the instrument.

Should it be found that aluminium is much preferable to steel for such indices, or that it were an object to dispense with the magnet, this may be accomplished by making the tube curved and placing it so that the mercurial piston may always be at the lowest point. Gentle tapping will then bring both indices into their initial position.

As to the scale, it will be observed that if the bore were accurately cylindrical, the degrees in the upper part would require to be shorter than those of the lower part, in consequence of the shortening which the column of air between the mercury and the piston must experience as the pressure upon it is increased; and such shortening could be easily determined geometrically. In practice, however, this may be made just to balance the conicity of the bore in such bores in thermometer tubing as are usually made; and a scale of equal parts may be applied to this thermometer, with as great likelihood of accuracy as in the ordinary instruments. By making the piston short enough its friction will be very small; and if the tube be perfectly dry, which it ought to be and must be in a good instrument, such a thermometer once in situ will serve for an indefinite time without going wrong.

XXII.—*Analysis of the Tunbridge Wells Water.*

BY JOHN THOMSON,

ASSISTANT IN THE ROYAL COLLEGE OF CHEMISTRY.

As it is now forty years since any analysis of the mineral water of Tunbridge Wells has been published, (the last being that by Sir Charles Scudamore, in 1816,) another investigation of the chemical composition of the celebrated Chalybeate Spring had become very desirable, the results being arranged in such a manner as to enable medical men to institute a correct comparison between this and other similar waters.

It was with this end in view, that the following analysis was undertaken:—

The spring, the only one that has been in use for many years, is situated at the east end of the Parade, and rises through an aperture the diameter of which is about $2\frac{3}{8}$ inches, into a marble basin having an extreme width of 2 feet 3 inches and a depth of 6 inches; over the side of this basin, the water flows into a channel connected with an outer basin which is open to the public, depositing in its progress a reddish brown precipitate of sesquioxide of iron. The side of the present basin, which has been in

use about nine years, is much corroded where the water overflows, from the action of the carbonic acid contained in the water. The temperature of the water as it issues from the spring is invariably 10° C. (50° F.) During the coldest winter, it has never been known to freeze in the basin. Sir Charles Scudamore says: on the 8th of February, 1816, when the atmosphere was at $-4\frac{1}{2}^{\circ}$ C. (24° F.) the water in the basin was still at 10° C. (50° F.) In the month of April, when I found some neighbouring springs yielding common water, and considered to be deep in their source, as low in temperature as 8° to $8\frac{1}{2}^{\circ}$ C. (46° and 47° F.) this spring was still at 10° C.

In two experiments made by myself on the 23rd of February and 17th of May of last year, the temperature was exactly 10° C. (50° F.) that of the air being on the former occasion $6\cdot7^{\circ}$ C. (44° F.) and on the latter $13\cdot3^{\circ}$ C. (56° F.)

The flow of the spring, according to the authority previously quoted, "was in August, 1815, in a minute, 1 quart 2 oz. and 5 drams. In the beginning of November, 1 quart. The summer had been unusually fine and dry. In October the season was wet. In the beginning of March, 1816, the supply was increased to 2 gallons and a half in a minute. At the end of this month, the quantity was lessened to 1 gallon and 7 pints. Much rain had fallen in the preceding months, but the winter had passed away with very little snow."

At the time the water was collected for the present analysis, viz. the 17th of May of last year, the mean of three experiments made by myself gave 15·13 litres = 3·33 gallons, as the flow of the spring in a minute.

A second series of experiments made on the 14th of April, of the present year, gave 14·21 litres = 3·13 gallons as the flow per minute.

The water, as it issues from the spring, is beautifully clear and transparent, and small bubbles of gas intermixed with occasional larger ones are continually rising to the surface. In taste and smell it is decidedly chalybeate, but not at all disagreeably so. Its specific gravity, compared with distilled water at $15\cdot5^{\circ}$ C = 60° F. is 1·00037. Blue litmus paper is slightly reddened by it, but on drying returns to its original colour; reddened litmus paper remains unchanged; tincture of violets when added to it instantly produces a greenish tint, which after the lapse of a few minutes becomes of a magnificent emerald green. I may here observe

that I have found this tincture the most delicate test for alkalinity, being more delicate than the most sensitive test-papers I have hitherto been able to procure.

By qualitative analysis it was found to contain protoxide of iron, protoxide of manganese, lime, magnesia, potassa, soda, sulphuric, hydrochloric, silicic and carbonic acids, together with a minute trace of organic matter.

Manganese was shown to be present, by fusing the iron precipitate supposed to contain it, with carbonate of soda and nitrate of potassa on platinum foil, when the well-known green colour of manganate of soda was produced. Also by treating a portion of the same precipitate with nitric acid and adding a small quantity of binocide of lead, when, as soon as the precipitate had subsided, the beautiful colour produced by permanganic acid was distinctly visible; but although both these tests gave very decisive results, the amount of manganese present was not sufficient for quantitative determination.

Bromine, iodine, and fluorine; nitric and phosphoric acids; arsenic, antimony and tin; alumina, strontia, lithia and ammonia, were tested for, but without success.

The methods made use of in testing for these substances, were the same as those employed by Dr. Hofmann, in his investigation of the chemical composition of the waters of Harrogate.*

By quantitative analysis, the following numbers were obtained:

Determination of iron —

| | Water employed. | Sesquioxide of iron obtained. | Sesquioxide of iron in 1000 parts. |
|----|-----------------|-------------------------------|------------------------------------|
| 1. | 2124.98 grms. | 0.085 | 0.0400 |
| 2. | 2124.98 „ | 0.079 | 0.0371 |
| | | | <hr/> |
| | | Mean | 0.03855 |

Determination of lime —

| | Water employed. | Carbonate of lime. | Lime in 1000 parts. |
|----|-----------------|--------------------|---------------------|
| 1. | 2000 grms. | 0.0565 | 0.0158 |
| 2. | 2124.98 „ | 0.0615 | 0.0161 |
| | | | <hr/> |
| | | Mean | 0.01595 |

* Quarterly Journal of the Chemical Society, vol. vii, p. 161.

Determination of magnesia —

| | Water employed. | Pyrophosphate of magnesia obtained. | Magnesia in 1000 parts. |
|------|-----------------|--|----------------------------|
| 1. | 2000 grms. | 0·0465 | 0·0083 |
| 2. | 1000 „ | 0·0195 | 0·0069 |
| Mean | | | 0·0076 |

Determination of the alkalies —

| | Water employed. | Mixed chlorides obtained. | Chlorides in 1000 parts. |
|------|-----------------|------------------------------|-----------------------------|
| 1. | 2000 grms. | 0·118 | 0·059 |
| 2. | 2000 „ | 0·115 | 0·057 |
| Mean | | | 0·058 |

Determination of potassa —

| | Water employed. | Chloride of potassium and platinum obtained. | Potassa in 1000 parts. |
|------|-----------------|---|---------------------------|
| 1. | 2000 grms. | 0·087 | 0·00837 |
| 2. | 2000 „ | 0·078 | 0·00750 |
| Mean | | | 0·00793 |

Determination of sulphuric acid —

| | Water employed. | Sulphate of baryta obtained. | Sulphuric acid in 1000 parts. |
|------|-----------------|---------------------------------|----------------------------------|
| 1. | 1000 grms. | 0·0515 | 0·0176 |
| 2. | 2000 „ | 0·1035 | 0·0177 |
| Mean | | | 0·01765 |

Determination of chlorine—

| | Water employed. | Silver salt obtained. | Chlorine in 1000 parts. |
|------|-----------------|-----------------------|-------------------------|
| 1. | 2000 grms. | 0·238 | 0·0294 |
| 2. | 1000 „ | 0·117 | 0·0289 |
| Mean | | | 0·02915 |

Determination of silica—

| | Water employed. | Silica obtained. | Silica in 1000 parts. |
|------|-----------------|------------------|-----------------------|
| 1. | 1000 grms. | 0·007 | 0·007 |
| 2. | 1000 „ | 0·008 | 0·008 |
| Mean | | | <u>0·0075</u> |

Determination of fixed residue—

| | Water employed. | Residue obtained. | Residue in 1000 parts. |
|------|-----------------|-------------------|------------------------|
| 1. | 1000 grms. | 0·17239 | 0·17239 |
| 2. | 1000 „ | 0·17089 | 0·17089 |
| Mean | | | <u>0·17164</u> |

Determination of carbonic acid—

To find the quantity of free carbonic acid contained in the water, a pipette of exactly known capacity was immersed in the spring, and the water thus obtained discharged into bottles containing a mixture of ammonia and chloride of calcium. The precipitate which formed, was collected, thoroughly washed, and the amount of carbonic acid contained in it estimated in the usual manner.

The same amount of water, viz., 2124·98 grms. was taken for each experiment.

| | Water employed. | Carbonic acid obtained. | Carbonic acid in 1000 parts. |
|------|-----------------|-------------------------|------------------------------|
| 1. | 2124·98 grms. | 0·345 | 0·16235 |
| 2. | 2124·98 „ | 0·355 | 0·16706 |
| Mean | | | <u>0·16470</u> |

| | |
|--|----------------|
| Total amount carbonic acid in 1000 parts | 0·16470 |
| Carbonic acid existing in combination | |
| With protoxide of iron | 0·02120 |
| With lime | 0·00282 |
| With magnesia | 0·00836 |
| With potassa | 0·00272 |
| Sum total | <u>0·03510</u> |
| Free carbonic acid remaining . . | <u>0·12960</u> |

From the preceding details it follows, that the chalybeate spring of Tunbridge Wells contains the following constituents in 1000 parts:—

| | |
|-------------------------------------|---------|
| Sulphate of lime | 0·03000 |
| Carbonate of lime | 0·00642 |
| Carbonate of magnesia | 0·01596 |
| Chloride of potassium | 0·00335 |
| Carbonate of potassa | 0·00854 |
| Chloride of sodium | 0·04540 |
| Carbonate of iron | 0·05589 |
| Carbonate of manganese | trace |
| Silica | 0·00750 |
| Organic matter | trace |
| Total | 0·17306 |
| Total residue (by experiment) . . . | 0·17164 |

Hence the weight of saline constituents contained respectively in 100 litres and a gallon of the water are as follows:

| | In 100 litres. | In an imp. gal. |
|----------------------------------|----------------|-----------------|
| Sulphate of lime | 3·0000 grms. | 2·1000 grains. |
| Carbonate of lime | 0·6420 „ | 0·4494 „ |
| Carbonate of magnesia | 1·5960 „ | 1·1172 „ |
| Chloride of potassium | 0·3350 „ | 0·2345 „ |
| Carbonate of potassa | 0·8540 „ | 0·5978 „ |
| Chloride of sodium | 4·5400 „ | 3·1780 „ |
| Carbonate of iron | 5·5890 „ | 3·9123 „ |
| Carbonate of manganese | trace „ | trace „ |
| Silica | 0·7500 „ | 0·5250 „ |
| Organic matter | trace „ | trace „ |
| | <hr/> 17·3060 | <hr/> 12·1142 |

Cubiccentim. Cubicin. in
in a litre. an imp. gal.

| | | |
|---|-------|-------|
| Amount of free carbonic acid at mean temperature and pressure | 69·35 | 19·19 |
|---|-------|-------|

In order to ascertain whether the amount of carbonic acid and iron contained by this water was subject to any considerable

variation, these were again determined in measured quantities of the water collected on the 14th of April of the present year. The results are given below.

| | Water employed. | Sesquioxide of iron obtained. | Sesquioxide of iron in 1000 parts. |
|------|-----------------|----------------------------------|---------------------------------------|
| 1. | 2124.98 | 0.077 | 0.03623 |
| 2. | 2124.98 | 0.075 | 0.03529 |
| Mean | | | 0.03576 |

| | Water employed. | Carbonic acid obtained. | Carbonic acid in 1000 parts. |
|------|-----------------|----------------------------|---------------------------------|
| 1. | 2124.98 | 0.345 | 0.16235 |
| 2. | 2124.98 | 0.362 | 0.17035 |
| Mean | | | 0.16635 |

These numbers are equivalent to 5.184 grms. in 100 litres or 3.6288 grains in the gallon of carbonate of protoxide of iron; and assuming the same amount of carbonic acid to exist in the combined state as in the preceding analyses, 70.23 cubic centimetres in a litre, or 19.44 cubic inches of this gas in a gallon of the water.

The chief characteristic of this water seems to be its extreme purity, its principal constituent being iron held in solution by the agency of free carbonic acid.

XXIII.—*Remarks on the Action of Heat on Gold, and its alloy with Copper.*

BY JAMES NAPIER, Esq.,

ASSAYER TO THE MEXICAN MINT.*

1st. *Action of heat on pure Gold.*—It appears to be a generally formed opinion, that pure gold, when exposed to a heat only sufficient to bring it to perfect fusion, does not lose in weight, and that to volatilize it, the heat of a powerful lens or that of the oxygen

* Communicated by R. D. Thomson, M. D.

blowpipe must be employed. The experiments of Kunkel and Gasto Caveus would appear to prove that such would be the case; both of these gentlemen state that, after keeping gold exposed to the highest heat of a glass furnace, the former for two months, and the latter for 30 weeks, there was no sensible alteration or diminution of weight. Mr. John A. Phillips, in his work on Metallurgy, states that "Gold fuses at a temperature estimated by Daniell at 2016° F., and when still more strongly heated, affords sensible metallic vapours;" but his authority is not given.

The experiments which I am about to record agree with the latter statement. I might mention that the gold employed for these experiments was that obtained by taking a portion of gold, mixing it with three times its weight of pure silver, cupelling with lead, and finally parting the silver by nitric acid. The gold thus prepared was melted in the following proportions, and the following results obtained:—

| No. | Weight of Gold used. Grains. | Time kept in fire. Hours. | Loss in weight. | Remarks. |
|-----|------------------------------|---------------------------|-----------------|--|
| 1 | 20 | 3 | 0.03 | No. 1. was weighed at the expiration of each hour, and lost exactly 0.01 gr. per hour. |
| 2 | 50 | 7 | 0.12 | |
| 3 | 100 | 6 | 0.11 | |
| 4 | 160 | 8 | 0.12 | |

These experiments do not show an exact uniformity of loss, but they prove that gold, even when pure, can be volatilized by the heat of a common furnace; the inequality of the results is easily accounted for by the inequality of the heat of the fire.

In the fourth of the above experiments, a most interesting result was obtained, and one which points out beyond doubt that gold is volatile when in fusion. The gold in this experiment was melted on a small fire-clay vessel, a cupel of bone-ash being inverted over it, and kept so during the whole time of fusion. On removing the whole from the fire, it was observed that the inverted cupel was tinged with a purple colour, and not only on the surface but to a little depth. The surface of this cupel was carefully examined with a strong lens, to see if there were any small shots of gold upon it; finding no shots, the purple colour was scraped off and assayed, by which means a small button of gold was obtained,

weighing 0·06 of a grain. This of course was only the one-half of what the button had lost altogether, as the junction between the small melting pot and the inverted cupel was not perfect and consequently some of the metallic vapour escaped; some of it was also deposited on the sides of the earthen crucible. In what state this gold passes off has not yet been determined; it must either be as an oxide (which is purple) or, if metallic, in the most minute particles, as not the slightest indication of metallic shot could be traced by means of a lens.

These experiments were many times repeated with nearly the same result each time.

2nd. *On the action of heat on the alloy of Gold and Copper.*—It is well known that the affinity between gold and copper is very great, and we find that when these two metals are melted together, and kept so for a short time, a quantity of the alloy passes off in the state of vapour. In coining gold coin, there is on a large coinage a considerable loss from this cause. I do not mean a large percentage; but where a large amount of the alloy is melted, the loss is considerable. The following experiments were made on a large scale, and they prove beyond all doubt the volatility of this alloy.

In pouring the alloy of gold and copper from the large black-lead crucibles (containing from 25 to 30 pounds) in which it was melted, there was observed a vapour rising from the mass, and as nothing more than the gold and copper which had the following composition —

| | |
|---------------------------|--------|
| Copper | 98·231 |
| Iron | 0·062 |
| Silver | 0·140 |
| Lead | 0·006 |
| Sulphur | 0·033 |
| Sand | 0·100 |
| Oxygen and loss | 1·428 |

100·000

was present, it was very certain that the alloy itself was passing off; to prove this the following simple method was adopted:

A common glass jar — used for collecting gases in the laboratory — was obtained, made wet inside with distilled water, and held about four inches over the crucible, as the alloy was in the act of being poured into the moulds; this occupied about one

minute of time. On removing the glass, it was entirely coated inside with small metallic globules, which were washed out with distilled water, dried, and examined with a lens; but by this means I could not tell whether the metal was oxide of copper or gold. The whole was then weighed and gave 4·80 grains, which was cupelled with lead on an ordinary bone-ash cupel, and there remained, after cupellation, a button of pure gold weighing 4·50 grains. To be perfectly convinced that there was no error in this experiment and the result obtained, the same routine was gone through a few days after, when the same result was obtained; the contents of the jar this time were 4·40 grains, which, when cupelled as before, gave a button of gold weighing 4·10 grains.

These results require no comment, as they speak for themselves; suffice it to say, that the greater the heat employed, the greater will be the loss; it is therefore important that the heat at which this alloy is melted be carefully regulated.

Another question now occurred to me, viz., how much pure gold is really lost when kept in fusion with different proportions of copper for a length of time? The experiments on this subject were made on a small scale in the laboratory.

The gold and copper were melted in small fire-clay pots in a common assay muffle, after remaining in fusion for the time mentioned in the following table. The pots were removed from the muffle and the buttons of alloy taken from the pots; the total loss was very great, from the volatilization of much of the copper; and as the surface of the alloy was not covered with carbonaceous matter, the copper oxidized rapidly; however, to obtain the real loss of pure gold was the object aimed at: to get this result, each button of alloy was mixed with $2\frac{1}{2}$ times its weight of silver (free from gold) cupelled with lead, and the silver then removed, by pure nitric acid in the usual manner of assaying these alloys, when a cornet of pure gold was obtained and the loss thus determined. The table gives the results obtained in this way.

| No. | Weight of Gold in grains. | Weight of Copper in grains. | Time in fusion. Hours. | Loss of Gold in grains. | Remarks. |
|-----|---------------------------|-----------------------------|------------------------|-------------------------|---|
| 1 | 100 | 12 | 6 | 0·234 | Heat only sufficient to melt the alloy. |
| 2 | 100 | 10 | 4 | 0·210 | } Heat a little greater than No. 1. |
| 3 | 100 | 20 | 4 | 0·450 | |
| 4 | 100 | 10 | 6 | 0·800 | As strong as could be obtained in the muffle. |

These results show that the greater the amount of copper and the greater the heat, the more gold is there lost, and that gold, when alloyed with copper, is more volatile than when alone, owing doubtless to the great affinity which these metals have for each other.

The small pots in which these different alloys were melted, were covered with inverted bone-ash cupels, each of which was tinged of a dark brown colour, mixed with purple. On scraping this colour from each of these cupels and reducing the metals, there was obtained from each a small button of gold weighing —

| | | |
|----------|-------|-------------|
| In No. 1 | 0.103 | of a grain. |
| „ 2 | 0.100 | „ |
| „ 3 | 0.261 | „ |
| „ 4 | 0.200 | „ |

These results do not show uniformity, as much of the vapour was lost, but they show not only that gold can be volatilized, but that it can even be caught and produced to prove its volatility.

I may mention that these experiments have been gone over repeatedly, and similar results have been obtained each time.

As a stronger proof of the great affinity existing between gold and copper, I will mention the two following experiments, made to ascertain whether an alloy of silver and gold, when fused and kept in that state for some time, would gain or lose in its proportion of gold.

1st. A small piece of silver, containing 1116 grains to every mark,* was introduced into a cupel, fused, and kept so for five hours, when it was removed and again assayed: it then contained 1141 grains of gold per mark, showing an increase of the gold to the extent of 25 grains per mark; thus showing that the silver which passed off, did not carry with it the same proportion of gold it originally contained.

2nd. There was obtained a piece of silver coin (a dollar), which was carefully assayed for gold, which metal it contained in the proportion of two grains per mark of coin; another piece of the very same coin was now fused and kept so for three hours, when it was once more assayed for gold, and it only contained an amount equal to half a grain to the mark of coin. From this it is perfectly

* The mark is equal to eight ounces.

evident that it was the copper contained in the coin passing off as oxide that took with it the gold, as we find that where no copper was present, the proportion of gold rose by fusion.

*Guananato Mint, Mexico,
March 20th, 1857.*

XXIV.—*On the separation of Iodine, Bromine, and Chlorine, and the comparative degree of affinity of these elements for Silver; with some analyses of their combinations with that metal occurring in Chili.*

BY FREDERICK FIELD, F. C. S.

ALTHOUGH both bromide and iodide of silver are decomposed by the action of chlorine at an elevated temperature, yet chloride of silver is completely decomposed by bromide of potassium, and both the bromide and chloride of silver by iodide of potassium. Even the action of hot strong hydrochloric acid has but little influence upon the iodide of silver, many days of continuous boiling being necessary for its entire decomposition. I believe that it has been the opinion of chemists that chlorine possesses an affinity for silver superior to all other elementary bodies, and we are told in Gmelin's Hand-book (vi, 144) that all salts of silver, even the insoluble ones, are converted into chloride by solutions of metallic chlorides. From the following experiments it appears to me that bromine has a greater affinity for silver than chlorine, and iodine a still greater affinity than bromine.

When a mixed solution of bromide of potassium and chloride of sodium is added gradually to a solution of nitrate of silver, *not in excess*, no trace of chloride of silver is precipitated, as long as any bromine remains in solution.

If, for example, one equivalent of nitrate of silver is dissolved in water, and one equivalent of bromide of potassium and one of chloride of sodium be added, the latter will be left quite intact, and bromide of silver and nitrate of potassa will alone be formed.

If, to a similar solution, iodide and bromide of potassium and chloride of sodium be added, iodide of silver and nitrate of potassa are formed, the bromide of potassium and chloride of sodium remaining undecomposed.

When bromide of potassium is poured upon chloride of silver, an entire decomposition ensues, bromide of silver and chloride of potassium being produced.

When iodide of potassium is added to chloride of silver, iodide of silver and chloride of potassium are formed — and when iodide of potassium is added to bromide of silver, there is a similar decomposition, the iodine replacing the bromine.

When chloride of silver in excess is agitated in a solution of iodide of potassium, and warmed for some hours, no trace of iodine can be detected in the solution: when, however, chloride of sodium is poured upon iodide of silver, no decomposition occurs, neither is there any action upon bromide of silver with the same salt; and when bromide of potassium is added to iodide of silver, there is no alteration in the union of the elements.

In the following experiments, all the reagents employed were perfectly pure. The iodide and bromide of potassium, and the chloride of sodium, were heated to expel mechanical water, until they ceased to lose in weight.

Ten grains of chloride of sodium were dissolved in water, and added to a solution of nitrate of silver, the latter being slightly in excess. The precipitated chloride was washed upon a filter, until no trace of the excess of silver could be detected by the addition of chloride of sodium to the filtrate. The chloride of silver was then washed into a beaker containing from 15 to 20 grains of bromide of potassium dissolved in two ounces of water. An immediate change of colour took place, the white chloride changing to the yellow of the bromide.

After digestion for about eight hours, the precipitate was filtered off, washed, dried, heated to incipient fusion and weighed.

Weight of Precipitate.

Calculated weight of Bromide.

32·04

32·09

32·04 grs. of bromide of silver contain 18·41 of silver; the substance in question gave 18·38 of silver.

10 grains of chloride of sodium were added to nitrate of silver, and the precipitate heated exactly as the former, iodide of potas-

sium being substituted for the bromide. After 10 hours' digestion the precipitate was weighed

| Weight of Precipitate. | Calculated weight of Iodide of Silver. |
|---|--|
| 40.17 | 40.13 |
| 40.17 Ag I = 18.46 Ag. Experiment furnished 18.44 Ag. | |

10 grains of bromide of potassium were added to a solution of nitrate of silver, the precipitate heated, as before, and washed into a solution of iodide of potassium.

| Weight of Precipitate. | Calculated weight of Iodide of Silver. |
|---|--|
| 19.71 | 19.73 |
| 19.71 Ag I = 9.03 Ag. Experiment furnished 9.05 Ag. | |

10 grains of bromide of potassium were converted into the bromide of silver, and this digested with a solution of chloride of sodium for 8 hours. It was then filtered, washed, dried, and weighed.

| Weight of Precipitate. | Weight of Bromide of Silver used. |
|------------------------|-----------------------------------|
| 15.77 | 15.78 |

showing that the bromide of silver was perfectly undecomposed. No trace of bromine could be detected in the filtrate.

10 grains of iodide of potassium were converted into the iodide of silver, and heated in the same manner, with chloride of sodium.

| Weight of Precipitate. | Weight of Iodide of Silver employed. |
|------------------------|--------------------------------------|
| 14.13 | 14.14 |

No trace of iodine was found in the solution.

All the above filtrates were severally tested for silver by passing a stream of hydrosulphuric acid through them for a considerable time. In one instance, the iodide of potassium added in rather great excess after filtration from the precipitated iodide of silver, exhibited a very faint brown tinge. The other remained unaffected.

From the foregoing results I deemed it possible that the separation of chlorine, iodine, and bromine, could be performed with great ease. The following experiments confirm this idea, although

the slight solubility of the precipitates in excess of the precipitants, when the latter are warm and concentrated, render great care necessary; considerable caution must also be employed by the manipulator with regard to the quantities he uses.

1st Experiment. 5 grains each of the iodide and bromide of potassium and chloride of sodium were dissolved in water, and precipitated by excess of nitrate of silver. The precipitate, after washing and heating until it began to fuse round the edges, weighed 27.19 grains (the theoretical number being 27.21): the same quantities of the three bodies were dissolved in another portion of water, precipitated as before with nitrate of silver, and the washed precipitate digested with a solution of bromide of potassium in the cold for about 10 hours. On washing and weighing the precipitate finally obtained, it was found to weigh 30.87 grains. As the difference between the equivalents of bromide of silver and chloride of silver (44.5) is to the equivalent of chloride of silver (143.6), so is the difference in weight after digesting in bromide of potassium, to the quantity of chloride of silver originally present. Thus, in the experiments referred to, 3.68 grains being the difference in weight of the precipitate after digestion,

$44.5 : 143.6 :: 3.68 : 11.86$ — Chloride of silver found.

The quantity of chloride of silver calculated from the 5 grains of chloride of sodium is 12.25 grains.

In the second experiment, the liquid was kept gently warmed during the operation, and the precipitate, after treatment, weighed 30.95 grains, which, by the rule above referred to, equals 12.13 grains of chloride of silver.

2nd Experiment. 5 grains of iodide and bromide of potassium and 5 grains of chloride of sodium were precipitated in the same manner, with nitrate of silver, and the precipitate was digested for 12 hours in a solution of iodide of potassium. The precipitate, after washing and incipient fusion, gave 36.83 grs.

As the difference of the equivalents of bromide and iodide of silver (47.1) is to the equivalent of bromide of silver (188.1), so is the excess in weight of the precipitate after digestion in iodide of potassium, to the weight of bromide of silver originally present.

In this experiment, therefore, the difference in weight of the

precipitate after digestion being 6.02 grs. the calculation is as follows :

$$47.1 : 188.1 :: 6.02 : 24.04$$

$$30.87 - 24.04 = 6.83 \text{ Ag I.}$$

Iodide of silver obtained from precipitation of the nitrate by 5 grains of iodide of potassium = 7.07.

By reversing the figures in the previous calculation of the chlorine and bromine, we can arrive at the quantity of bromide of silver, after deducting the quantity of iodide of silver found in the subsequent experiments.

The following is a table showing the results by calculation and analysis.

| Experiment. | Theory. |
|------------------------|------------------------|
| 5 grs. KI = 6.83 Ag I. | 5 grs. KI = 7.06 Ag I. |
| „ KBr = 8.26 AgBr. | „ KBr = 7.87 AgBr. |
| „ NaCl = 11.86 AgCl. | „ NaCl = 12.25 AgCl. |

We have therefore the following quantities of iodine, bromine, and chlorine by experiment and calculation, as deduced from the silver salts.

| Experiment. | Theory. |
|---------------|---------|
| Iodine 3.69 | 3.81 |
| Bromine 3.51 | 3.34 |
| Chlorine 2.92 | 3.02 |

and the quantities of iodide, bromide, and chloride calculated from the silver-salts, are as follows :

| Experiment. | Theory. |
|-------------|--------------|
| 4.85 KI | 5 grs. KI. |
| 5.23 KBr | 5 grs. KBr. |
| 4.84 NaCl | 5 grs. NaCl. |
| <hr/> 14.92 | <hr/> 15.00 |

Although by the description, the above method may appear long and tedious, the actual experiment is not so. After weighing three equal portions of the salts to be analysed, they are placed in three flasks with ground glass stoppers and about an ounce of water is added to each; nitrate of silver being then added, slightly

in excess to the three, the stoppers are replaced, and each flask agitated violently. The precipitates subside in a few minutes, leaving the supernatant fluid perfectly clear. They are then filtered through separate funnels and washed with hot water. No. 1 is dried and weighed. No. 2 is digested in bromide of potassium, dried and weighed, and No. 3 in iodide of potassium, dried and weighed.

Although the results above stated are not very far from the truth, more experiments are necessary, before this method can be admitted into quantitative analysis. The great fear, as already stated, is, that the solutions of the liquids in which the silver compounds are digested should be made too concentrated, in which case the latter are dissolved to some slight extent, even in the cold. By preliminary experiments on the part of the analyst, and a knowledge of the quantities of the substance taken, great excess may of course be avoided.

By this method, some analyses were made of the iodide, bromide, bromo-chloride, and chloride of silver found native in the district of Chañarcillo, in the province of Atacama, South America.

The specimens analysed were collected by myself from the mines. M. Domeyko has analysed many of the compounds in question, and his results form an interesting paper in the "Annales des Mines." Colonel Yorke has also examined a specimen of chloro-bromide brought to England by Admiral Seymour, an account of which was published in the Quarterly Journal of the Chemical Society.

Pure chloride of silver, when freshly taken from the mine, is perfectly colourless, and can be cut with a knife into slices resembling horn, which are quite transparent. On exposure to the sun, it soon assumes a dark purple tint. This mineral is rarer than is generally imagined. The large quantities extracted from the mines, and which, after crushing, are submitted to direct amalgamation, consist principally of chloro-bromides. A specimen of chlorides from the "Republicana Mine," yielded by analysis—

Silver 75·27

Chlorine 24·73

100·00 or AgCl.

Chloro-bromide of Silver, No. 1. This mineral has a pale green colour, and is little acted upon by light. The specimen analysed

occurred as a sectile mass, associated with a red ferruginous ore and carbonate of lime from the "Colorade Mine," Chañarcillo.

| Experiment. | | Theory. |
|-------------|-------|---------|
| Silver | 68.22 | 68.231 |
| Bromine | 16.84 | 16.831 |
| Chlorine | 14.92 | 14.938 |
| <hr/> | | <hr/> |
| 99.98 | | 100.000 |

Chloro-bromide of Silver, No. 2. This mineral possesses a darker colour than the former variety, and is the most abundant of all the species. It is the principal source of the silver from the district of Chañarcillo, many tons being annually extracted from the mines; it seldom occurs crystallised, and is generally found in masses or small veins traversing ferruginous ore, with carbonate of lime. An analysis yielded —

| Experiment. | | Theory. |
|-------------|-------|---------|
| Silver | 66.94 | 66.972 |
| Bromine | 19.82 | 19.830 |
| Chlorine | 13.18 | 13.198 |
| <hr/> | | <hr/> |
| 99.94 | | 100.000 |

Chloride of silver 53.38

Bromide of silver 46.62

100.000 or 3 AgCl.2AgBr.

Chloro-bromide of Silver, No. 3. This is a very dark green mineral, having sometimes a rich purple tint, not so abundant as the former. I have found it in a copper mine in minute crystals upon silicate of copper.

| Experiment. | | Theory. |
|-------------|-------|---------|
| Silver | 61.07 | 61.08 |
| Bromine | 33.82 | 33.90 |
| Chlorine | 5.00 | 5.02 |
| <hr/> | | <hr/> |
| 99.89 | | 100.00 |

Chloride of silver 20.28

Bromide of silver 79.72

100.00 or AgCl.3AgBr.

Bromide of Silver. This very rare mineral, lately described under the name of Bromylite, in Dana's Mineralogy, has only been found, I believe, in one mine in Chili. The former minerals, described as bromide of silver in earlier editions, are very distinct from the pure variety, possessing, it is said, a green colour. Their composition is probably $3\text{AgBr} + \text{AgCl}$. The specimen I obtained consists of splendid octohedra of considerable size, imbedded singly in a mass of pure carbonate of lime, through which a vein of pure silver is running—and has a very beautiful appearance. The crystals, as to colour and lustre, exactly resemble amber, and, after being cut and polished, are much harder than the bromo-chlorides or chloride, and appear to be little affected by light. An analysis of one of the crystals yielded —

| | |
|----------------|-------|
| Silver . . | 57.43 |
| Bromine . . | 42.57 |
| <hr/> | |
| 100.00 or AgBr | |

Iodide of Silver. This mineral, although it has been found both in the province of Coquimbo and Copiapo in Chili, as well as in Mexico, must be considered rare. It has the same appearance, as to colour, &c., as the artificially prepared compound. On heating it with sulphuric acid and peroxide of manganese, the violet vapours of iodine are immediately perceptible. A specimen from Delirio's Mine, Chañarcillo afforded —

| | |
|----------------|-------|
| Silver . . | 45.98 |
| Iodine . . | 54.02 |
| <hr/> | |
| 100.00 or AgI. | |

I have not yet analysed any other variety. The iodides and bromides I believe are unknown. To sum up the above varieties, we have —

| | |
|-----------------------|-----------------------------|
| Chloride of silver | AgCl |
| Chloro-bromide of do. | $2\text{AgCl}.\text{AgBr}$ |
| Do. of do. | $3\text{AgCl}.2\text{AgBr}$ |
| Do. of do. | $\text{AgCl}.3\text{AgBr}$ |
| Bromide of do. | AgBr |
| Iodide of do. | AgI |

To refer for a moment to a former portion of this paper, all the native chloro-bromides and chlorides of silver are capable of decomposing iodide of potassium.

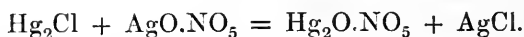
Although it is impossible to conceive a denser mineral than the chloride of silver, yet slices of it, if placed in a solution of iodide of potassium, become instantly coated with iodide of silver, and in a few weeks all traces of iodine have disappeared from the liquid.

The mineral veins in Chañarcillo possess an intense interest to the Geologist and Mineralogist. Without entering for an instant into the discussion of the formation of veins in the earth, I may mention that shells, untouched by the action of fire, with colours nearly fresh, have been found in Chañarcillo, from the half opened orifice of which metallic silver was separating.

By a careful analysis of the rock (free from metal) which forms the walls of the lode, I hope perhaps to detect iodine, chlorine, and bromine. As it seldom or never rains in these districts, soluble salts are untouched, even on the surface of the earth.

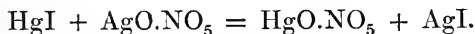
Crystallised Chloride of Silver. Löwig has shown that chloride of silver is soluble to a considerable extent in nitrate of mercury, and crystallises as the solution cools, in octohedra. When solutions of nitrate of silver and corrosive sublimate are mixed together, a precipitate of chloride of silver is formed, which, on boiling with the nitrate of mercury produced by the double decomposition, is partially dissolved, and the solution, after filtration, deposits chloride of silver in small crystalline grains. These crystals, after washing with water until no trace of mercury passes, and exposed to the sun's rays, do not blacken like the ordinary chloride. They furnished on analysis, results corresponding exactly with the composition of pure chloride of silver; they were perfectly soluble in ammonia. A considerable quantity was prepared and exposed moist to the direct rays of the sun for a month, and remained unaltered in appearance. I propose to call this interesting body, *allotropic chloride of silver*.

When sub-chloride of mercury (calomel) is boiled with nitrate of silver, chloride of silver and sub-nitrate of mercury are obtained; the former salt is not soluble in solutions of the latter.



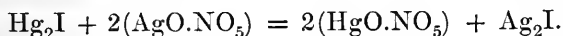
I have observed however in some instances, a black precipitate on the addition of nitrate of silver to calomel, which disappears on boiling. This reaction still requires elucidation.

Crystallised Iodide of Silver. This beautiful compound may be prepared by boiling red iodide of mercury with slight excess of nitrate of silver, and filtering; the nitrate of mercury formed by decomposition dissolves the iodide of silver, which separates as the solution cools, in brilliant crystalline plates. These crystals, like the allotropic chloride, do not change colour by exposure to light:



If great excess of nitrate of silver be employed, the compound $\text{AgO.NO}_5 + \text{AgI}$, discovered by Preuss, is formed, which crystallises in white needles. This can be avoided, and the pure iodide obtained by having the solution dilute.

I endeavoured, by long-continued boiling of nitrate of silver upon sub-iodide of mercury, to form a sub-iodide of silver (a salt unknown at present) imagining that perhaps the following decomposition would take place:—



After 36 hours' ebullition, a pale lemon-coloured powder was formed, which yielded more silver than the ordinary iodide, and a small quantity of protonitrate of mercury remained in solution. After precipitation with hydrochloric acid and addition of iodide of potassium, a decided red precipitate was formed. However, no definite compound was obtained; the decomposition appeared to be as follows:—



and therefore analagous to that of the sub-chloride of mercury with nitrate of silver.

XXV.—On a New Series of Organo-Thionic Acids.

By JOHN THOMAS HOBSON, Ph. D.

DALTON SCHOLAR AT OWEN'S COLLEGE, MANCHESTER,

SECOND MEMOIR.

IN a former memoir* under the above title, after describing the preparation and properties of ethylotrithionic acid, together with

* Journal of the Chemical Society, x. p. 55.

the analysis of several of its salts, I mentioned that a preliminary experiment had been made, which showed, that by acting upon zinc-methyl, with sulphurous acid, a white crystalline body was produced, as was the case with zinc-ethyl; and at the same time I expressed a hope that this body on analysis, would prove to be the zinc salt of the first acid of the trithionic series, viz. the Methylotrithionic acid; such, however, I find, is not the case, for the body on investigation proved to be an acid of a different molecular composition, united with oxide of zinc.

To prepare this substance in large quantities, the following plan was adopted. A quantity of zinc-methyl, prepared by digesting iodide of methyl with zinc for several hours, at a temperature of 130°C , in the copper digester, and according to the plan recommended by Professor Frankland* for the production of zinc-ethyl, was subjected in a flask to a rapid stream of sulphurous acid, evolved from sulphuric acid and copper turnings, the gas being perfectly dried before admission to the zinc-methyl, by passing through a Woulf's bottle of concentrated sulphuric acid. On connecting the sulphurous acid generator, with the flask containing the zinc-methyl, the gas was very rapidly absorbed; and unless the flask was kept quite cold, the contents commenced boiling, owing to the heat produced by the energetic action which took place between the sulphurous acid and zinc-methyl. After the lapse of a short time, large quantities of a white crystalline body appeared in the flask containing the zinc-methyl.

The iodide of methyl before conversion into zinc methyl, was mixed with about two and-a-half times its volume of ether, so that the zinc-methyl which was obtained, was in a moderately dilute state, which enabled the sulphurous acid more thoroughly to act upon it; indeed the re-action was so complete, that every trace of zinc-methyl was decomposed, the body obtained not effervescing with water, neither could any excess of oxide of zinc be precipitated from it, by carbonic acid, as was the case in the corresponding reaction with zinc-ethyl. A portion of the compound prepared as above described, after the ether had been distilled off, was exposed for a short time in vacuo, to get rid of the last traces of ether, and also of any sulphurous acid that might be mechanically retained in its pores, when it presented the appearance of a white amorphous mass, insoluble in alcohol and ether, but very soluble in water; no well defined crystals, however, could be obtained by the evapora-

* Transactions of the Royal Society for 1855, p. 259.

tion of an aqueous solution of the salt; and as carbonic acid did not precipitate any oxide of zinc from it, and no other method of purification suggesting itself to me, I determined to analyse the body in its crude state. It yielded the following results;

- I. 3.025 grs., burnt with oxide of copper, a tube of peroxide of lead being interposed between the chloride of calcium tube, and potash bulbs, gave 1.198 grs. of carbonic acid, and 0.644 grs. of water.
- II. 10.443 grs., similarly treated, gave 4.08 grs. of carbonic acid, and 2.70 grs. of water.
- III. 3.195 grs., burnt with a mixture of carbonate of magnesia and chlorate of potash, the product dissolved in hydrochloric acid, and precipitated with chloride of barium, gave 6.605 grs. of sulphate of baryta.
- IV. 4.325 grs., similarly treated, gave 9.061 grs. of sulphate of baryta.
- V. 7.162 grs., precipitated boiling by carbonate of soda, the precipitated basic carbonate of zinc, washed, dried, and ignited, gave 2.594 grs. of oxide of zinc.
- VI. 10.045 grs., similarly treated, gave 3.618 grs. of oxide of zinc.

These results, as will be seen from the following calculation, agree with the formula $\text{ZnO}, \text{S}_2 \left\{ \begin{array}{l} \text{C}_2\text{H}_3 \\ \text{O}_3 \end{array} \right.$

| Calculated. | | | Analyses. | | | | | | |
|----------------|-------|--------|-----------|-------|-------|-------|-------|-------|--------|
| | | | 1. | 2. | 3. | 4. | 5. | 6. | Mean. |
| C ₂ | 12.0 | 10.76 | 10.79 | 10.65 | — | — | — | — | 10.72 |
| H ³ | 3.0 | 2.69 | 2.36 | 2.87 | — | — | — | — | 2.61 |
| Zn | 32.5 | 29.15 | — | — | — | — | 29.05 | 28.89 | 28.97 |
| S ₂ | 32.0 | 28.70 | — | — | 28.36 | 28.74 | — | — | 28.55 |
| O [†] | 32.0 | 28.70 | — | — | — | — | — | — | 29.15 |
| | <hr/> | <hr/> | | | | | | | |
| | 111.5 | 100.00 | | | | | | | 100.00 |

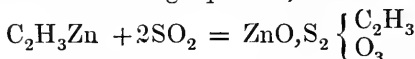
This substance is therefore, evidently, the zinc salt of an acid formed by the substitution of one equivalent of oxygen, in every two equivalents of sulphurous acid, by the radical methyl.

The name for this acid, in accordance with the nomenclature that I adopted in the case of ethylotrithionic acid,* will be *Methylodithionic acid*.

The formation of methylodithionate of zinc, from the action of

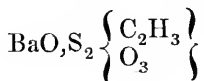
* Journal of the Chemical Society, x. p. 55.

zinc-methyl upon sulphurous acid, is very simple, and will be easily understood from the following equation,



Methylodithionate of zinc is colorless, inodorous, very soluble in water, but insoluble both in alcohol and ether. It possesses a disagreeable and somewhat bitter taste. It is not decomposed by heating to 100° C, but at a few degrees higher it blackens, evolving fumes with a most offensive odour. On evaporating an aqueous solution of this salt, it gradually crystallises out as the liquid becomes very concentrated, but no large crystals of it could be obtained, owing to its great solubility.

METHYLODITHIONATE OF BARYTA.



This salt is most easily prepared, by adding to a solution of methylodithionate of zinc, caustic baryta in excess, filtering off from the precipitated oxide of zinc, and passing carbonic acid through the filtrate to precipitate the excess of baryta; on again filtering and evaporating in a water-bath, the salt is obtained in a state of purity.

Methylodithionate of baryta thus prepared, is a colorless, inodorous, crystalline body, insoluble both in alcohol and ether, but very soluble in water. It is precipitated from a concentrated aqueous solution by alcohol, as a white granular powder. It is perfectly neutral to test paper. This salt by the spontaneous evaporation of a concentrated aqueous solution in vacuo, crystallises in the regular system, the crystals being cubes arranged in an octahedron. Methylodithionate of baryta does not decompose even if heated to 170° C; when dried at 100° C it yielded the following analytical results:

- I. 7.45 grs., burnt with chromate of lead, gave 2.16 grs. of carbonic acid, and 1.50 grs. of water.
- II. 10.18 grs., burnt with a mixture of chromate of lead, and oxide of copper, gave 2.89 grs. of carbonic acid, and 2.015 grs. of water.*

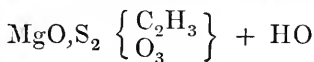
* Analyses II, III, VII, VIII, were made from well formed crystals of this salt, freed from the mother liquor by pressure between blotting paper, and dried at 100°C. The other analyses were made from the salt, obtained by evaporating an aqueous solution to dryness in a water-bath.

- III. 9.23 grs., similarly treated, and a stream of oxygen passed over at the end of the combustion, gave 2.69 grs. of carbonic acid, and 1.74 grs. of water.
- IV. 6.788 grs., dissolved in water, and the baryta precipitated with dilute sulphuric acid, gave 5.325 grs. of sulphate of baryta.
- V. 4.796 grs., similarly treated, gave 3.775 grs. of sulphate of baryta.
- VI. 6.16 grs., gave 4.835 grs. of sulphate of baryta.
- VII. 11.87 grs., gave 9.40 grs. of sulphate of baryta.
- VIII. 6.06 grs., burnt with a mixture of carbonate of magnesia and chlorate of potash, the product dissolved in hydrochloric acid, and precipitated with chloride of barium, gave 9.65 grs. of sulphate of baryta.
- IX. 6.50 grs., similarly treated, gave 10.225 grs. of sulphate of baryta.
- X. 3.99 grs., gave 6.28 grs. of sulphate of baryta.

These numbers, as will be seen by the following calculation, agree very closely with the above formula.

| Calculated. | | | Analyses. | | | | | | | | | | |
|----------------|-------|--------|-----------|-------|------|-------|-------|-------|-------|-------|-------|-------|--------|
| | | | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | Mean. |
| C ₂ | 12 | 8.13 | 7.91 | 7.74 | 7.94 | — | — | — | — | — | — | — | 7.86 |
| H ₃ | 3 | 2.03 | 2.23 | H2.19 | 2.19 | — | — | — | — | — | — | — | 2.17 |
| Ba | 68.6 | 46.48 | — | — | — | 46.14 | 46.32 | 46.18 | 46.59 | — | — | — | 46.30 |
| S ₂ | 32 | 21.68 | — | — | — | — | — | — | — | 21.85 | 21.58 | 21.56 | 21.66 |
| O ₄ | 32 | 21.68 | — | — | — | — | — | — | — | — | — | — | 22.01 |
| | 147.6 | 100.00 | | | | | | | | | | | 160.00 |

METHYLODITHIONATE OF MAGNESIA.



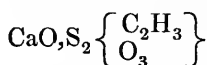
This salt can either be prepared by the double decomposition of the baryta salt and sulphate of magnesia, or by precipitating the zinc from methylodithionate of zinc, by caustic magnesia. The salt which was analysed, was prepared by the decomposition of the baryta salt; it is a colorless, inodorous body, and like all the other salts of methylodithionic acid, it is insoluble in alcohol and ether, but very soluble in water. On evaporating its aqueous solution, the salt is obtained as a mass of minute crystals, which after dessication at 100° C still retain one equivalent of water. They yielded on analysis the following numbers;

- I. 7.175 grs., burnt with oxide of copper, gave 3.065 grs. of carbonic acid, and 2.585 grs. of water.

- II. 5.53 grs., dissolved in water and precipitated with ammonia and phosphate of soda, the precipitate washed, dried, and ignited, gave 3.105 grs. of pyrophosphate of magnesia.
- III. 4.88 grs., similarly treated, gave 2.73 grs. of pyrophosphate of magnesia.
- IV. 4.29 grs., ignited with carbonate of magnesia, and chlorate of potash, the product dissolved in hydrochloric acid, and precipitated with chloride of barium, gave 9.84 grs. of sulphate of baryta,
- agreeing, as will be seen from the following percentage calculation, with the above formula,

| Calculated. | | Analyses. | | | | |
|----------------|-----|-----------|-------|-------|-------|--------|
| | | 1. | 2. | 3. | 4. | |
| C ₂ | 12 | 11.64 | — | — | — | 11.64 |
| H ₄ | 4 | 4.00 | — | — | — | 4.00 |
| Mg | 12 | — | 12.03 | 11.98 | — | 12.00 |
| S ₂ | 32 | — | — | — | 31.47 | 31.47 |
| O ₅ | 40 | — | — | — | — | 40.89 |
| | 100 | | | | | 100.00 |

METHYLODITHIONATE OF LIME.



This salt is best prepared by adding lime-water in excess to methylodithionate of zinc, filtering off from the oxide of zinc, and passing carbonic acid through the filtrate, to precipitate the excess of lime. On exposing a concentrated solution of this salt *in vacuo*, it gradually dried up to a solid mass, but owing to its solubility, no crystals could be obtained. Methylodithionate of lime is insoluble both in alcohol and ether, it is perfectly inodorous, and possesses a disagreeable and somewhat bitter taste; after drying at 100°C, it yielded the following analytical results:

- I. 5.16 grs., burnt with oxide of copper, gave 2.27 grs. of carbonic acid, and 1.53 grs. of water.
- II. 7.78 grs., dissolved in water and precipitated with oxalate of ammonia and ammonia, the precipitate washed, dried and ignited, gave 3.882 grs. of carbonate of lime.

These numbers agree with the above formula, as will be seen from the following percentage calculation.

| Calculated. | | | Analyses. | |
|----------------|-------|-------|-----------|-------|
| | | | 1. | 2. |
| C ₂ | 12 | 12·12 | 12·00 | — |
| H ₃ | 3 | 2·03 | 3·29 | — |
| Ca | 20 | 20·20 | — | 19·64 |
| S ₂ | 32 | 32·32 | — | — |
| O ₄ | 32 | 32·32 | — | — |
| | <hr/> | <hr/> | | |
| | 99 | 99·99 | | |

METHYLODITHIONIC ACID.

The method adopted for the preparation of this acid in its free state, was the precipitation of the baryta, from methylo-dithionate of baryta, by dilute sulphuric acid. By these means a liquid was obtained, which reddened blue litmus, possessed a feebly acid taste, and dissolved carbonate of silver slowly; the acid liquid thus produced, was however, very instable, decomposing with a deposition of sulphur in a short time, even in a very dilute solution; so that no salt of methylo-dithionic acid, with the exception of that of silver, was prepared directly from the acid in its free state.

METHYLODITHIONIC ETHER.

This ether was prepared by distilling a mixture of methylo-dithionate of baryta and sulphovinate of potash. The reaction which occurred between these bodies, did not take place until they were strongly heated, when an oily liquid, accompanied with large quantities of sulphurous acid, distilled over. This liquid, after being washed with water, dried by standing over chloride of calcium, and redistilled in vacuo, presented the appearance of a light straw-colored liquid, with a peculiar fishy smell, and slightly heavier than water; on analysis, however, this ether did not yield results from which a formula could be safely deduced, the temperature required to produce it being so high, that it had probably undergone partial decomposition.

METHYLODITHIONATE OF SILVER

Was prepared by treating carbonate of silver with the free acid, prepared as above. On attempting to evaporate a solution of this salt in a water-bath, it was decomposed even before the water commenced boiling. Light also rapidly acts on this body, a dilute solution blackening very quickly if exposed to daylight. It could not, therefore, be obtained in a fit state for analysis. In regard to

stability, this salt presented a striking contrast to Ethylo-trithionate of silver, which is remarkably stable.

METHYLODITHIONATE OF COPPER

Can be prepared by the double decomposition of methylo-dithionate of baryta, and sulphate of copper. Its aqueous solution has a bright green color, which on evaporation at 100° C becomes brownish yellow, owing to the decomposition of the salt; indeed this compound is so very instable, that a dilute solution of it, exposed to the atmosphere at its common temperature, gradually decomposes, sulphur being deposited.

METHYLODITHIONATE OF NIKEL

Is prepared like methylo-dithionate of copper, substituting sulphate of nickel for sulphate of copper. Its solution is of a grass-green color. This salt could not be obtained in a solid form; for on allowing an aqueous solution of it spontaneously to evaporate in vacuo, it dried up to an amorphous, dirty, buff-colored mass, the salt, during the evaporation, having been partially decomposed.

In a former memoir* on the subject of "Organo-Thionic-Acids," the results of the action of sulphurous acid on zinc-ethyl are described, and from the analysis of the compound produced, I was led to regard it, as the zinc salt of an acid, formed by the replacement of one atom of oxygen, in three of sulphurous acid, by ethyl; now ethyl and methyl, being members of the same homologous series, and it being an almost established rule that when we get a body in one of these series, we may predict the existence of its homologue in the other, I expected that by acting upon zinc-methyl under the same conditions as on zinc-ethyl, I should obtain an acid molecularly similar to the ethyl acid, having methyl in the place of ethyl. That such is not the case will be seen from the foregoing analyses, the reaction instead of taking place between one equivalent of zinc-methyl and three of sulphurous acid, having occurred between one of zinc-methyl, and two of sulphurous acid.

The want of homology in these acids is very singular, and might almost lead to the conclusion, that by acting with sulphurous acid, on the zinc compounds of the homologous series, commencing with methyl, we should have one equivalent more of sulphurous acid taking part in the reaction for every increase of C_2H_2 , thus, if the

* Journal of the Chemical Society, x. 55.

body zinc-hydrogen were known, it would probably commence this series of acids, by replacing one equivalent of oxygen in one equivalent of sulphurous acid, by hydrogen.

I have not yet been able to try the action of sulphurous acid on zinc-amyl, which would decide this point, but hope on some future occasion to communicate to the society, the results of this reaction. The acid formed from zinc-amyl, should it exist, would, according

to the supposition mentioned above, have the formula $S_6 \left\{ \begin{smallmatrix} C_{10}H_{11} \\ O_{11} \end{smallmatrix} \right\}$

The following is a list of the names and formulæ of the bodies which have been described in this memoir ;

| | |
|--------------------------------|--|
| Methylo-dithionate of Zinc | $ZnO, S_2 \left\{ \begin{smallmatrix} C_2H_3 \\ O_3 \end{smallmatrix} \right\}$ |
| Methylo-dithionate of Baryta | $BaO, S_2 \left\{ \begin{smallmatrix} C_2H_3 \\ O_3 \end{smallmatrix} \right\}$ |
| Methylo-dithionate of Magnesia | $MgO, S_2 \left\{ \begin{smallmatrix} C_2H_3 \\ O_3 \end{smallmatrix} \right\} + HO$ |
| Methylo-dithionate of Lime | $CaO, S_2 \left\{ \begin{smallmatrix} C_2H_3 \\ O_3 \end{smallmatrix} \right\}$ |

XXVI.—*Some Chemical Facts respecting the Atmosphere of Dwelling-houses.*

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THE following communication contains the results of an investigation carried on for the purpose of supplying chemical data respecting the warming and ventilating of private dwelling-houses, including barracks, under a Commission appointed for that purpose by the General Board of Health.

The atmosphere of a closed inhabited space is rendered unfit for continued respiration long before the greater part of the oxygen has disappeared. The presence of mere traces of the products of combustion is sufficient to produce an unhealthy atmosphere, even when almost the normal amount of the active constituent is present. It is, therefore, by the quantity of impurities introduced into the air and not by a diminution of the oxygen that we are best able to judge of the capability of such an atmosphere to support healthy animal life.

The conditions of deterioration which render the supply of fresh air necessary to living animals inhabiting closed spaces, are:

1. The presence of an excessive quantity of the oxides of carbon and other poisonous gases.
2. The presence of either too large or too small a quantity of aqueous vapour dissolved in the air.
3. The presence of organic putrescent bodies, effluvia, proceeding from decomposing animal or vegetable matter.
4. Inconvenient elevation of temperature, arising from the heat of combustion.

The existence of any one of these four sources of deterioration in the air, in which animals dwell for any length of time, is injurious to the health of such animals. In general, however, these four conditions of insalubrity occur together, and an efficient system of ventilation must, therefore, 1st, free the air from the excess of the products of the oxidation of carbon; 2ndly, adjust the proper equilibrium between the air and the dissolved aqueous vapour; 3rdly, carry off completely all putrescent organic matter disseminated through the air; and 4thly, establish an agreeable mean temperature.

In order to determine how we can best diminish the quantity of carbonic acid produced in a closed space by the respiration of animals, and the combustion of illuminating bodies, we must know how much carbonic acid is evolved by the animals inhabiting the spaces under consideration, and by the substances used for illuminating purposes; and also how small a quantity of the oxides of carbon affects the health of such animals. The best experimental data concerning the first of these points we obtain from the researches of Scharling, who determined the amounts of carbonic acid exhaled by various individuals under the normal conditions of pressure, temperature, &c. Scharling found that the mean quantity of carbonic acid given off by an adult man per hour amounted to 34.8 grammes, or 17.52 litres (1069.2 cubic inches). An indirect method of obtaining the amount of expired carbonic acid from the total volume of respired air and its known percentage of carbonic acid, gives rather a larger number for the quantity of carbonic acid evolved per head per hour, viz., 22.08 litres (1348 cubic inches) (Vierordt, Hutchinson). The mean of these two volumes, or 19.8 litres (1208 cubic inches) may, therefore, be taken as representing the maximum quantity of carbonic acid evolved per head per hour.

The exact determination of the second point is at present impossible, from the absence of any direct experimental facts upon which a conclusion might be based. It is, however, generally admitted, that air containing more than 1 per cent. of carbonic acid is injurious, and that air containing more than 0·5 per cent, is likewise hurtful if breathed for any length of time (Leblanc. Peclét). Reid and Arnott give a much lower limit to the non-injurious effects of this gas; but these statements have not been verified by exact experiment. Hence it is at present premature to say that the smallest increase above the normal amount (4 in 10,000) is not productive of harm, and therefore no limit can be fixed at which the carbonic acid becomes innocuous; the object of ventilation in this particular being to diminish the quantity of carbonic acid as much as possible below the limit admitted to be hurtful, without incurring other unpleasant effects arising from draughts, air, or reduction of temperature. It would nevertheless appear impossible, by any system of ventilation, to reduce the quantity of carbonic acid contained in an inhabited closed space to the proportion found in the free atmosphere.

Carbonic oxide acts as a much more violent poison on the animal body than carbonic acid; an atmosphere containing 1 per cent. of the former gas being immediately fatal to animal life, whilst respiration can be continued, although with difficulty, in air containing from 4 to 5 per cent. of the latter gas; hence, every trace of carbonic oxide, arising from a possible entrance of the products of the combustion of heating materials, must be immediately removed.

The average amount of aqueous vapour dissolved in the free atmosphere throughout the year is about 75 per cent. of the saturating quantity (Müller); hence we may conclude that in artificially heated spaces, the proportion of aqueous vapour should not vary much from this amount. This is borne out by practice; for in heating the House of Lords the conditions under which an agreeable atmosphere, as regards aqueous vapour, is found to exist, are when the difference between the wet and dry-bulb thermometers, at a mean temperature of $17\cdot8^{\circ}\text{C}$, is more than $1\cdot7^{\circ}\text{C}$, and less than 5°C , corresponding to an amount of watery vapour varying from 82 to 55 per cent. on the saturating quantity.

The third cause of deterioration in an inhabited confined atmosphere, viz., the presence of organic putrescent matters, animal effluvia, is one which for the present we are unable to estimate chemically, and, therefore as, *ceteris paribus*, the amount

of carbonic acid evolved from oxidation of the animal body must be proportional to the quantity of decomposing organic matter, we must; for the present, take the carbonic acid as representing deterioration both from respiration and from putrescent exhalation.

The opinions regarding the quantity of air required for the healthy continuance of respiration are, as has been stated, very various. Upon purely practical and experimental grounds Péclet (*Traité de la Chaleur*) concludes that each man requires 5 cubic feet per minute. His conclusions are based, 1st., upon the amount of air which it was found necessary to admit, in order to exclude all closeness and smell from schools, and 2ndly, upon the amount of air, at the mean atmospheric temperature, and half saturated with aqueous vapour, which became saturated by the moisture given off from the body. The minimum quantity of air which a man should receive per minute, is according to Vierordt, $2\frac{1}{2}$ cubic feet; Dr. Reid advises 10 cubic feet, and Dr. Arnott considers 20 cubic feet necessary. From the following experiments in barrack and school-rooms, I have come to the conclusion that 10 cubic feet per minute per head is insufficient to remove all effluvia, and to diminish the carbonic acid to a satisfactory minimum limit, and that probably at least 20 cubic feet per head per minute is necessary to remove completely the organic putrescent matter, at least in the case of soldiers' sleeping-rooms.

The amount of ventilation required in a room of a given size, occupied by a given number of persons, must naturally partly depend upon the duration of the occupation, although in most cases an equilibrium between the produced and escaping carbonic acid is soon established.

The various sources from which a supply of fresh air is obtained, may be divided into two classes; 1st, natural, or accidental sources, or means of access of air not solely employed for the purpose of ventilation, such as chimneys, windows, walls, doors, &c.; 2ndly, artificial, or special sources, or means employed for the direct object of increasing the supply of air.

The present incomplete state of the whole subject of ventilation, depends in great measure on the want of precise information on two fundamental points. We have already considered the first of these, viz., when is, and when is not a closed inhabited space unhealthy? to this question no definite answer can be given. The second point upon which our knowledge is equally defective relates to the amount of exchange of air which we obtain from the acci-

dental sources under all possible conditions. Until we know exactly when an atmosphere is unhealthy, and can determine how much fresh air enters, and deteriorated air issues from our windows, doors, and chimneys, under given circumstances, we cannot expect that the subject of ventilation should assume a definite form.

The determination of the first of these defective points involves a laborious investigation in physiological chemistry; and the full examination of the second point also entails an extended series of determinations, of which the results would be valuable and trustworthy only when the experimental data had increased to a very large amount.

I have been unable, up to the present time, to enter at all fully into this latter most important fundamental question. I have merely made one series of determinations which may serve to show the interesting facts which might be obtained from a more extended experimental enquiry.

EXPERIMENT I.

A quantity of carbonic acid was evolved in a room of 2,560 cubic feet capacity, containing no fire and a closed flue, and all doors (four) and windows (two) were shut. The carbonic acid contained in the inclosed air was then determined at consecutive half-hours. The following are the experimental data:—Temp. of air, 11° l. Barometric pressure, 0.7546^m.

| | at 0 ^h 0' | at 0 ^h 30' | at 1 ^h 0' | at 1 ^h 30' |
|-----------------------------------|----------------------|-----------------------|----------------------|-----------------------|
| Weight of carbonic acid obtained. | gm. 0.0135 | gm. 0.0062 | gm. 0.0058 | gm. 0.0058 |
| Volume of water escaping. | 1 litre | 1 litre | 1 litre | 1 litre |

| | at 0 ^h 0' | at 0 ^h 30' | at 1 ^h 0' | at 1 ^h 30' |
|---|----------------------|-----------------------|----------------------|-----------------------|
| Volume of carbonic acid in 1000 of air. | 7.207 | 3.310 | 3.099 | 3.099 |

It is thus seen that the carbonic acid diminishes in half an hour from 0·7 to 0·3 per cent. of the total volume of air although all direct ventilation was checked. After the first half-hour the amount of carbonic acid remained constant, possibly from the continued respiration of two persons in the confined atmosphere. The exchange of carbonic acid through close windows, doors, and walls appears from this experiment to be very great.*

In order to form some idea of the amount of gaseous diffusion which takes place through brick and mortar walls, I have determined the quantity of carbonic acid which diffuses through a common brick. For this purpose a brick was cemented with pitch into the end of a box, 3 feet long and 9 inches broad, by $4\frac{1}{2}$ inches deep. The interior of the box was lined with pitch, and carbonic acid was led into the box by means of two tubes cemented into the sides. After the box had stood for some minutes to allow the gas to diffuse equally throughout the space, a sample of the contained atmosphere was collected, by allowing the air in the box to enter a gas-collecting tube previously filled with mercury. The carbonic acid contained in the samples of air thus collected in consecutive hours was determined eudiometrically. In order to exclude an error, arising from a possible leakage of the box, a second series of analyses were made in the same way, with the exception that the whole brick was covered with a layer of pitch, and thus the leakage determined. The following table gives the result of the analysis.

EXPERIMENT II.

A. *Determination of diffusive interchange through brick.*

1. Collected directly after filling.

| | Vol. | Pressure. | °C | Vol. at 0°C and 0·76 pressure. |
|---------------------------------------|-------|-----------|------|--------------------------------|
| Vol. of gas employed . | 122·1 | 0·7410 | 10·2 | 114·8 |
| After absorption of CO ² . | 102·8 | 0·7320 | 10·2 | 95·4 |

* In confirmation of this fact, I may state that a perfectly analogous result was obtained independently by Professor Pettenkofer in Munich.

2. Collected after standing one hour.

| | | | | |
|---------------------------------------|-------|--------|------|------|
| Vol. of gas employed . | 104.3 | 0.7243 | 10.2 | 95.6 |
| After absorption of CO ² . | 89.1 | 0.7196 | 7.7 | 82.0 |

3. Collected after standing two hours.

| | | | | |
|---------------------------------------|-------|--------|-----|------|
| Vol. of gas employed . | 104.3 | 0.7268 | 7.7 | 96.9 |
| After absorption of CO ² . | 92.5 | 0.7206 | 8.5 | 85.1 |

B. *Control experiment with pitched brick.*

1. Collected directly after filling.

| | Vol. | Pressure. | °C | Vol. at 0°C and 0.76 pressure. |
|---------------------------------------|------|-----------|-----|-----------------------------------|
| Vol. of gas employed . | 92.7 | 0.7053 | 6.6 | 84.0 |
| After absorption of CO ² . | 79.5 | 0.6974 | 5.3 | 71.6 |

2. Collected after standing three hours.

| | | | | |
|---------------------------------------|-------|--------|-----|-------|
| Vol. of gas employed . | 115.6 | 0.7233 | 6.0 | 107.7 |
| After absorption of CO ² . | 101.6 | 0.7235 | 7.0 | 94.3 |

From experiment A we have,

Sample 1 contained 16.96 per cent. of carbonic acid.

„ 2 „ 14.22 „ „ „

„ 3 „ 12.17 „ „ „

Hence the loss of carbonic acid in 1st hour was 2.74 per cent.

„ „ „ „ 2nd „ 2.05 „

„ „ „ „ in two hours 4.79

From experiment B we find that in two hours a leakage of 1.54 per cent. of carbonic acid occurred. Hence the amount of carbonic acid which diffused through the brick was in two hours $4.79 - 1.54 = 3.25$ per cent. on a total of 16 per cent. of carbonic

acid. That is, when a closed space contained 16 per cent. of carbonic acid, more than 3 per cent. escaped through a solid brick in two hours.

The beneficial action of our brick and mortar walls is therefore, not merely confined to taking up or giving off moisture to the air, for they are eminently hygroscopic, but an actual and very large diffusive interchange goes on within the pores of the brick and mortar, so that our walls become a most important aid to ventilation. Of course the kind of surface covering which the walls possess, will materially influence the amount of diffusion which takes place through them, but the well-known unhealthiness of iron or new and damp houses, may probably to some extent be accounted for by the absence of all diffusive interchange through the wet walls. Owing to the impossibility of estimating the animal effluvia in inhabited spaces, the following experiments consist chiefly of carbonic acid determinations, together with estimation of dissolved aqueous vapour, and in one instance a determination of the traces of carbonic oxide and hydrocarbons present in the confined atmosphere.

By means of a large aspirator, a known volume of air V , under a known pressure P , and at a known temperature t , can be drawn over a system of weighed tubes, alternately filled with pumice-stone steeped in sulphuric acid and potash. The two tubes furthest from the aspirator contained sulphuric acid for the purpose of drying the air, the next two tubes contained hydrate of potash in a soft spongy mass to absorb the carbonic acid, and the next two tubes contained sulphuric acid to retain any moisture taken from the potash. The volume of dry air V_1 at 0° and 0.76, is found from the following equation, in which p signifies the tension of aqueous vapours at t° C.

$$V_1 = \frac{V(P - p)}{(1 + 0.00366t) 0.76}$$

The volume of carbonic acid at 0° C. and 0.76 met. is found in cubic centimetres by multiplying the weight of carbonic acid found in grammes by 503.27, the volume in cub. cent. of 1 gramme of carbonic acid at the normal temperature and barometric pressure.

In order to test the accuracy of the method, a determination was made of the carbonic acid contained in the free air of London on a windy day, February 27, 1857.

Experiment gave the following results :

EXPERIMENT III.

| | | |
|--|--------|--------|
| Weight of carbonic acid obtained . . . | 0.0308 | gram. |
| „ dissolved aqueous vapour . . . | 0.2410 | „ |
| Volume of aspirated air . . . | 43.2 | litres |
| Atmospheric temperature . . . | 8° | C. |
| Barometric pressure . . . | 0.7725 | m |

Hence we have :

Volume of air at 0° and 0.76 . . . 42.28 litres.

Carbonic acid . . „ „ . . . 15.50 cub. cent.

or in 10,000 volumes of air 3.7 of carbonic acid.

The amount of carbonic acid found by Saussure (Pogg. Ann. XIX. 391) in the free atmosphere at Chambeisy, on the Lake of Geneva, was 3.8 in 10,000 as a mean of 17 experiments.

In order still more fully to test the trustworthiness of the method, I made use in Experiment No. V of twice as large an absorbing surface of potash as that previously and subsequently employed. The results of this analysis shows that the whole of the carbonic acid is withdrawn by two potash tubes.

The first carbonic acid determinations in closed inhabited spaces were made at the Wellington Barracks, in the rooms in which the men were sleeping.

EXPERIMENT IV.

Wellington Barracks. House B, room 16. Capacity of room 7,920 cubic feet. Carbonic acid collected after 16 men had occupied the room for 6 hours. (9^h. P.M.—3^h.A.M.) All ventilators, except one over fire-place, closed. Common wide grate; dimensions of chimney 6 feet from floor, 1 foot 4 by 9 inches. All doors and windows shut. Low fire in grate during experiment. Air collected 2 feet 6 inches from floor, at height of men's heads when in bed.

| | | |
|--|------------------------|--------|
| Weight of carbonic acid obtained . . . | 0.0985 | gram. |
| „ aqueous vapour . . . | 0.3438 | „ |
| Volume of aspirated air . . . | 42 | litres |
| Duration of the experiment . . . | 2 ^{hrs} . 26' | |
| Temperature of air . . . | 15° | C. |
| Barometric pressure . . . | 0.775 | m. |

Hence we have :

| | |
|------------------------------------|------------------|
| Volume of air at 0°C. and 0.76 met | . 39.93 litres |
| „ carbonic acid | 49.58 cub. cent. |

or in 10,000 volumes of air, there are 12.42 volumes of carbonic acid

The amount of aqueous vapour found was 8.61 grammes per cubic metre. From the observations of the wet and dry-bulb thermometer, wet 13°2 C—dry 16°8 C; the amount of aqueous vapour is calculated to be 8.9 grammes per cubic metre. Hence the air of the soldiers' sleeping-room contained 66.2 per cent. of the saturating quantity of aqueous vapour.

Chemical method of determining the amount of ventilation.

We have assumed that a man exhales 0.686 cubic feet of carbonic acid per hour. Hence 16 men will exhale 65.86 cubic feet in 6 hours. We now require to know with what quantity of air must this 65.86 cubic feet of carbonic acid be mixed, so that the percentage of this gas should amount to 0.1242, that is, the quantity found in the barrack-room.

As the free atmosphere contains carbonic acid, we must add more air than we should need were it free from that gas.

If V represent the volume of pure air which must be added, and A the fraction which the impurity in the air (0.04) is of the limit of impurity in the mixture (0.1242), the volumes of air (V_1) which must be added, is found from the expression.

$$V_1 = V + Va + Va^2 + \dots Va^n$$

The three first terms of this series are all that need be considered.

In this way it is found that in order to reduce 65.86 cubic feet of carbonic acid to 0.1242 of the total bulk, we require 76,600 cubic feet of air. That is, in 6 hours 76,600 cubic feet of air pass through the room and carry off 0.1242 per cent. of its bulk of carbonic acid. This gives to each man a volume of 13.3 cubic feet per minute, a quantity insufficient to remove completely all animal effluvia.

Physical method of determining the amount of ventilation.

The quantity of air issuing from any chimney can be calculated, when the mean temperature and the dimensions of the chimney are known.

Temp. of outer air 9° C.

Mean temp. of chimney 31° C.

Height of chimney 57 feet.

Area of chimney-pot 60 square inches.

From these data a volume of 35 cubic feet of air is found to issue from the chimney per minute.

From this determination it would seem that only a portion of the deteriorated air is carried off by the chimney draught, the larger proportion escaping by the other accidental sources of ventilation, viz., windows, doors, and walls

EXPERIMENT V.

Wellington Barracks. Conditions in every respect the same as in the previous experiment. Double the usual number of potash-tubes were employed.

| | | |
|----------------------------------|----------------------------|-----------------|
| Weight of carbonic acid obtained | . 0.0810 | gram. |
| „ water | „ . 0.2653 | „ |
| Vol. of aspirated air | . . . 36 | litres. |
| Duration of the experiment | . . . 2 ^h 0' | |
| Temp. of air | . . . 14° 9 | C. |
| Barometric pressure | . . . 0.776 ^m . | |
| Wet bulb therm. | 11° 2 | Dry ditto 14° 7 |

Hence we have :

Vol. of carbonic acid at 0° & 0.76 40.77 cub. cent.

„ air 34.29 litres.

or in 10,000 volumes of air 11.89 vols. of carbonic acid.

The quantity of aqueous vapour found was 7.74 grms. per cubic metre; the thermometrical observations giving 8.3 grms. per cubic metre

From this determination it is seen that under like conditions the quantity of carbonic acid, and consequently the amount of ventilation remains constant on two consecutive nights.

EXPERIMENT VI.

In order to determine the increase in the carbonic acid produced by a crowded state of the room, 4 additional men slept in the room, on another occasion, making a total of 20 men, and the carbonic acid was estimated as before. The presence of a trace of carbonic oxide or hydro-carbons was also detected by passing the air, deprived of moisture and carbonic acid, over ignited oxide of copper, and collecting the carbonic acid and water formed. The other conditions, as to stoppage of artificial ventilation, &c. &c., remained the same as in Experiment IV.

| | | |
|--|--------------------|---------|
| Weight of carbonic acid obtained . . . | 0.0801 | gram. |
| Weight of CO ² & HO from CO & C ⁿ H ⁿ . . . | 0.0102 | „ |
| Volume of aspirated air | 30 | litres. |
| Temp. of air 12°5 C. Barometric pressure | 0.764 ^m | |
| Wet bulb thermometer 8°4 Dry ditto | 11°7 | |

Hence :

| | | |
|--|-------|------------|
| Vol. of carbonic acid at 0° & 0.76 . . . | 40.32 | cub. cent. |
| „ air | 28.43 | litres. |

or in 10,000 volumes air 14.18 vols. carbonic acid.

The volume of carbonic oxide and marsh gas corresponding to the volume of water and carbonic acid obtained is found to be about 1 part in 10,000.

The most important conclusions which we may draw from these determinations are, that even in cold weather, an insufficient ventilation is obtained in the soldiers' sleeping rooms by means of accidental sources of fresh air, and of the chimney draught occasioned by a small fire. In the summer when the difference between the temperature of the outer and the inclosed air becomes very small, the ventilation by chimneys and windows alone will become more inefficient.

In order to determine how far the natural or accidental sources of ventilation supply the necessary exchange of air, in cases in which the production of carbonic acid is more rapid, several determinations were made in crowded school-rooms in which the direct access of fresh air was more or less checked.

EXPERIMENT VII.

Large day-school for boys. Capacity of room 22,140 cub. ft. Number of boys present 164. Imperfect ventilation from stove-flue, and accidental sources. Determination made after the room had been occupied for 2½ hours.

| | | |
|--|--------------------|---------|
| Weight of carbonic acid obtained . . . | 0.0519 | gram. |
| Vol. of aspirated air | 12 | litres. |
| Temp. of air 18°C. Barometric pressure | 0.759 ^m | |
| Wet bulb therm. 16° 7. Dry ditto | 19° 1 | |

Hence :

| | | |
|--|-------|------------|
| Vol. of carbonic acid at 0° & 0.76 . . . | 26.12 | cub. cent. |
| „ air | 11.01 | litres. |

or in 10,000 volumes of air 23.71 volumes of carbonic acid. This corresponds to an allowance of 330 cubic feet of air per head per

hour (calculated as in Experiment IV) or less than 6 cubic feet per minute.

The aqueous vapour amounted to 12 grms. per cubic metre or 75.0 per cent. on the saturating quantity.

EXPERIMENT VIII.

The carbonic acid contained in the atmosphere of a crowded school-room, having a capacity of 4,640 cubic feet, and containing 67 boys, was next determined. The only means of exchange of air consisted in a chimney draught and accidental openings from windows, doors, &c.

| | | |
|----------------------------------|---------------------|---------------------|
| Weight of carbonic acid obtained | . . . | 0.0687 gm. |
| Volume of aspirated air | | 12 litres. |
| Temp. of air 12° C. | Barometric pressure | 0.7478 ^m |
| Wet bulb therm. 10°6. | Dry ditto | . 12°4 C. |

Hence :

Volume of carbonic acid at 0° & 0.76 . 34.57 cub. cent.

„ air 11.15 litres.

or 10,000 volumes air contain 31.00 vols. of carbonic acid. This represents an amount of ventilation of 240 cubic feet per head per hour, or only 4 cubic feet per minute.

Hence it is seen that the accidental sources of ventilation are quite inadequate to furnish the requisite amount of exchange of air in the case of crowded schools.

The next point to which I directed my attention was the distribution of carbonic acid throughout inhabited spaces, ventilated by a chimney draught together with windows, doors, &c.

It has been stated that in common, unventilated dwelling-rooms, the heated carbonic acid formed by respiration, and combustion of illuminating substances, on ascending accumulates in the upper parts of such rooms, not being removed by the current of fresh air entering by the doors and windows, and issuing by the fire-place into the chimney. A permanent atmosphere rich in carbonic acid is thus supposed to exist in all inhabited rooms, not artificially ventilated at top, and persons breathing the air above the level of the chimney opening were conceived to be respiring an unhealthy air, whilst children breathing below that level, were asserted to be consuming a healthy air, free from any excessive quantity of carbonic acid.

This supposition is rendered extremely doubtful by two purely theoretical considerations.

1. The known laws of expansion of gases by heat.

2. The known laws of the diffusion of gases.

Experiment, both chemical and physical, has most fully confirmed this theoretical presumption, and has proved that in ordinary dwelling-rooms, even in the exaggerated form of crowded school-rooms, the above causes are quite sufficient to equalize, throughout the closed space, the amount of carbonic acid formed by respiration; that in fact the atmospheres of such inclosed spaces are homogeneous as regards the contained carbonic acid.

A series of valuable observations made on the direction and force of the currents in the atmosphere of a heated room has been lately made for the Commission on Warming and Ventilating Private Dwellings, by Mr. J. F. Campbell, the Assistant Secretary of the Board of Health. Mr. Campbell determined the effects produced on the atmosphere of a closed room by the radiant heat from a fire, by means of thin filaments of floss-silk placed in regular position, throughout the space to be examined. The observations thus conducted, show, that a continual and rapid circulation of the air takes place throughout the inclosed space; the rarified atmosphere in front of the fire rising rapidly, with a force of from 14 to 30 grains per square foot, as measured by Mr. Campbell, and spreading out along the ceiling in the direction of the cooling surfaces of the walls and windows, where it immediately falls, and is carried again forward to the fire to supply the place of the expanded air rising to the ceiling.

In order to obtain chemical evidence regarding the homogeneous nature of the inclosed atmosphere, simultaneous carbonic acid determinations were made in the air collected above and below the level of the chimney opening in several unventilated rooms.

EXPERIMENT IX.

The first simultaneous carbonic acid determination in the air of two different parts of a closed unventilated space, was made in a small room inhabited by a costermonger's family.

Capacity of room 950 cub. ft., containing 9 persons. Chimney draught from small fire, together with accidental sources the only means of ventilation.

A.—Air collected 6 inches from ceiling in centre of room.

Weight of carbonic acid obtained . . . 0·0266 gm.

Vol. of aspirated air 12 litres.

Temp. of air 16° C. Barometric pressure 0·7425^m

Hence we have :

Vol. of carbonic acid at 0° & 0·76 . . . 14·09 cub. cent.

„ air 11·03 litres.

or in 10,000 vols. air 12·13 vols. carbonic acid.

B.—Air collected 2½ feet from floor below level of the opening of chimney-flue.

Weight of carbonic acid obtained . . . 0·0280 gm.

Vol. of aspirated air 12 litres.

Temp. of air 16°. Barometric pressure. 0·7425^m

Hence :

Vol. of carbonic acid at 0° & 0·76 . . . 14·09 cub. cent.

„ air. 11·03

or in 10,000 vols. of air 12·76 vols. carbonic acid.

EXPERIMENT X.

Crowded school-room. Capacity 4640 cubic feet. Number of boys 70. Temperature of air 14°5. Barometric pressure 0·7427^m. Ventilation from chimney flue and accidental openings.

A.—Air collected 6 inches from ceiling.

Weight of carbonic acid obtained . . . 0·0719 gm.

Vol. of aspirated air 12 litres.

Hence :

Vol. of carbonic acid at 0° & 0·76 . . . 36·19 cub. cent.

„ air 10·95 litres.

or, in 10,000 vols. air 33·05 carbonic acid.

B.—Air collected 3 feet from floor—below level of chimney-piece—
—at level of boys' heads when sitting.

Weight of carbonic acid obtained . . . 0·0708 gm.

Vol. of aspirated air 12 litres.

Hence :

Vol. of carbonic acid at 6° & 0·76 . . . 35·63 cub. cent.

„ air 10·95 litres.

or, in 10,000 vols. of air 32·53 vols. carbonic acid.

EXPERIMENT XI.

A second determination in the same locality, under similar circumstances.

Temperature of air $12^{\circ}5$. Barometric pressure $0\cdot7627^m$.

A.—Collected, 6 inches from ceiling.

Weight of carbonic acid obtained . . . $0\cdot0539$ gram.

Vol. of aspirated air 12 litres.

Hence we have:

Vol. of carbonic acid at 0° & $0\cdot76$. . . $27\cdot12$ cub. cent.

„ air $11\cdot35$ litres.

or, in 10,000 air, $23\cdot9$ volumes of carbonic acid.

B.—Collected, $2\frac{1}{2}$ feet from floor.

Weight of carbonic acid obtained . . . $0\cdot0555$ gram.

Vol. of aspirated air 12 litres.

Hence:

Vol. of carbonic acid at 0° & $0\cdot76$. . . $27\cdot93$ cub. cent.

„ air $11\cdot35$ litres.

or, in 10,000 vols. air $24\cdot59$ vols. carbonic acid.

EXPERIMENT XII.

Simultaneous carbonic acid determinations made in a large and more crowded school-room (for dimensions, &c. see Expt. VII.)

Temperature of air 15° . Barometric pressure $0\cdot7485^m$.

A.—Air collected, 6 inches from ceiling.

Weight of carbonic acid obtained . . . $0\cdot0590$ gram.

Vol. of aspirated air 12 litres.

Hence:

Vol. of carbonic acid at 0° & $0\cdot76$. . . $29\cdot69$ cub. cent.

„ air $11\cdot01$ litres.

or in 10,000 vols. air $26\cdot96$ vols. carbonic acid.

B.—Air collected 3 feet from floor.

Weight of carbonic acid obtained . . . $0\cdot0645$ gram.

Vol. of aspirated air 12 litres.

Hence:

Vol. of carbonic acid at 0° & $0\cdot76$. . . $32\cdot46$ cub. cent.

„ air $11\cdot01$ litres.

or in 10,000 air $29\cdot49$ vols. carbonic acid.

EXPERIMENT XIII.

Simultaneous carbonic acid determinations made at the Wellington Barracks. Room of similar dimensions as in previous experiments. Supplied with Arnott's stove and ventilator; both flue and ventilator fully open. Fire nearly out, 20 men in room. Other conditions as before.

Atmospheric temperature $16^{\circ}0$. Barometric pres. $0\cdot7640^m$.

A.—Air collected 3 inches from ceiling.

Weight of carbonic acid obtained . $0\cdot0308$ grm.

Vol. of aspirated air 12 litres.

Hence :

Vol. of carbonic acid at 0° & $0\cdot76$. $15\cdot50$ cub. cent.

„ air $11\cdot20$ litres.

or in 10,000 vols. air $13\cdot82$ vols. carbonic acid.

B.—Air collected $2\frac{1}{2}$ feet from floor.

Weight of carbonic acid obtained . $0\cdot0375$ grm.

Vol. of aspirated air 12 litres.

Hence :

Vol. of carbonic acid at 0° & $0\cdot76$. $18\cdot87$ cub. cent.

„ air $11\cdot20$ litres.

or in 10,000 vols. air $16\cdot84$ vols. carbonic acid.

From these determinations it is seen that in inhabited dwelling-rooms or school-rooms, the carbonic acid is distributed equally throughout the atmosphere, the small differences arising not only from the errors of experiment, but also from the slightly varying composition of the currents of air passing over the point at which the air was collected.

In order to determine the influence which a considerable elevation of temperature, from the combustion of large quantities of gas and the respiration of a number of persons, exerted upon the distribution of carbonic acid, two simultaneous determinations were made in the air from the pit and gallery of a fashionable crowded theatre.

EXPERIMENT XIV.

By means of a system of tubes, the air was collected at a height of 4 feet above the stage over the stalls, and also at a distance of 30 feet directly above the first position in the front of the gallery.

Temperature of the air 23° C. Barometric pressure 0·7376^m.

A.—Air collected 34 feet above stage.

Weight of carbonic acid obtained . . . 0·0444 grm.

Vol. of air aspirated . . . 8 litres.

Hence :

Vol. of carbonic acid at 0° & 0·76 . . . 22·34 cub. cent.

„ air . . . 6·96 litres.

or in 10,000 volumes of air 32·12 vols. carbonic acid.

B.—Air collected 4 feet above the stage

Weight of carbonic acid obtained . . . 0·0547 grm.

Vol. of aspirated air . . . 12 litres

Hence :

Vol. of carbonic acid at 0° & 0·76 . . . 27·53 cub. cent.

„ air . . . 10·44 litres.

or in 10,000 volumes air 26·37 carbonic acid.

Here, as would naturally be expected, a great difference is found to exist between the amount of carbonic acid contained in the lower and in the higher layers of air.

The following tables give the results of the foregoing experiments.

TABLE I.

RESULTS OF CARBONIC ACID DETERMINATIONS IN VARIOUS LOCALITIES.

| Number and Locality of Experiment. | Carbonic acid found in 1000 volumes of air. | Cubic capacity of closed space. | Number of persons contained. | Number of cubic feet of air per head per hour. | Amount of aqueous vapour saturating quantity = 100. |
|--|---|---------------------------------|------------------------------|--|---|
| Experiment III. Normal Air . | 0·37 | — | — | — | 65·5 |
| Experiment IV. Wellington Barracks | 1·242 | cub. ft. 7920 | 16 | cub. ft. 13·3 | 66·2 |
| Experiment V. Wellington Barracks | 1·189 | 7920 | 16 | 13·0 | 59·5 |
| Experiment VI. Wellington Barracks | 1·418 | 7920 | 20 | — | 65·0 |
| Experiment VII. Large School Room . | 2·371 | 22140 | 164 | 6 | 75·0 |
| Experiment VIII. School Room . | 3·100 | 4640 | 67 | 4 | 74·0 |

TABLE II.

DISTRIBUTION OF CARBONIC ACID IN DWELLING ROOMS, ETC.

| Number and Locality of Experiment. | Carbonic acid in 1000 vols. air. | | Deviation from mean. | Cubic capacity of room. | Number of persons. |
|---|----------------------------------|------------------------------|----------------------|-------------------------|--------------------|
| | collected 6 inches from ceiling. | collected 2½ ft. from floor. | | | |
| Experiment IX. Small Dwelling Room | 1·213 | 1·276 | — + 0·031 | 940 | 9 |
| Experiment X. School Room | 3·305 | 3·253 | + — 0·016 | 4640 | 70 |
| Experiment XI. Ditto | 2·390 | 2·459 | — + 0·034 | 4640 | 70 |
| Experiment XII. Larger School Room | 2·696 | 2·948 | — + 0·126 | 22140 | 160 |
| Experiment XIII. Wellington Barracks | 1·382 | 1·684 | — + 0·152 | 7920 | 20 |
| Experiment XIV. Crowded Theatre | 30 ft. from stage 3·212 | 4 ft. from stage 2·637 | + — 0·287 | not determined. | |

XXVII.—APPENDIX TO PAPER

“On some Points in the Composition of Wheat-Grain, its Products in the Mill, and Bread.”

(See pp. 1—55.)

By J. B. LAWES, F.R.S., F.C.S., AND

J. H. GILBERT, PH.D., F.C.S.

ON the assumption that it is established by others (for we have not ourselves any direct experiments on the point), that the loss of dry substance, by the panary fermentation, is less than one, and, perhaps, less than 0·5 per cent. of that of the flour employed, it is obvious that the number of loaves of a given weight obtained from a sack of flour (280 lbs.) being given, and the per-centage of water in the flour also known, we could easily estimate, within very narrow limits, the per-centage of dry substance in the bread produced. The per-centage of dry matter in bread, thus determined by calculation from the actual or assumed amount in the flour, will be too high by the unknown quantity lost by fermentation, and too

low by the amount of salt, or other saline matter, added. On the latter point it may be stated, that about 4 lbs. of salt to the sack of flour is equal to about 1 per cent. in the bread. Indeed, assuming the loss by fermentation as above, and taking such data as we possess as to the usual amount of mineral matter added by the baker, we are disposed to conclude, that the dry matter in bread, calculated as above supposed from the amount of dry substance in flour, and the amount of bread it yields, would be too low by from 0·5—1 per cent., depending on the quantity of the extraneous mineral matter used.

Again, if the whole of the loss by the changes during fermentation be less than 0·5 per cent., and if these, as is known to be the case, mainly affect the non-nitrogenous constituents, we can, in the same way as for the dry matter and the water, estimate pretty exactly the amount of *nitrogen*, or of *nitrogenous compounds*, from the amount of the one or the other in the flour employed.

Frequently, however, the estimates which are given by one and the same authority, for the composition of wheaten-flour and bread respectively, do not seem to bear a proper relation to each other. We have thought, therefore, that it might be useful to give, as an appendix to our paper, a tabular form, showing the yield of bread from 100 of flour, and the per-centages of dry matter, water, nitrogen, or nitrogenous compounds, in the former—assuming any given number of four-pound loaves to be obtained from a sack of flour, and assuming also given probable amounts of water and of nitrogen in the flour. This is accordingly done in Table XVI., which follows.

We need only further say that, with fermented baker's bread of good quality, ninety-five *really four-pound loaves* to the sack of flour is a yield perhaps very seldom reached.* It would appear, however, from published statements, that of unfermented bread, more than 100 four-pound loaves may be obtained from the sack of flour. It is worthy of remark, that if this be the case, and if the loss by the fermentative process be really so small as is now supposed, the gain in weight by the non-fermenting method, is only a gain of *water retained in the bread*. Unless, therefore, the unfermented bread be better adapted for digestion or assimilation, or be sold at a correspondingly lower price, the consumer will be a considerable loser by the purchase of the unfermented loaf.

* We speak of course of *pure wheaten bread*.

TABLE XVI.

Showing the Composition of Wheaten Bread, calculated from the Quantity of Bread obtained from a given Weight of Flour, and from the Composition of the Flour.*

| Equal to Bread for 100 Flour. | Per Cent. Dry Matter and Water in the Bread. | | | | | | Per Cent. Nitrogen, or Nitrogenous Compounds (Gluten, Albumen, &c.), in Bread. (Nitrogenous Compounds=Nitrogen×6.3). | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| | If 16 per Cent. Water in Flour. | | | If 15 per Cent. Water in Flour. | | | If 14 per Cent. Water in Flour. | | | If 1.65 Nitrogen (=10.4 Nit. Compound) per Cent. in Flour. | | | If 1.7 Nitrogen (=10.7 Nit. Compound) per cent. in Flour. | | | If 1.75 Nitrogen (=11.0 Nit. Compound) per Cent. in Flour. | | | If 1.8 Nitrogen (=11.3 Nit. Compound) per Cent. in Flour. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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* The Figures in the Table should, of course, be taken subject to the qualifying remarks which have been made. It is obvious that the Form can easily be extended to include any further or intermediate ranges of produce of bread, or composition of flour.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.

On the Application of Sewage to Agriculture.*

By Dugald Campbell, Esq., F.C.S.

THE object of the following report is in the first place to attempt an exposition of the actual nature of the problem involved in the utilization of sewage for agricultural purposes, as it appears from a chemical point of view. For this purpose I shall have to request your attention to some points of what may be termed the Chemical History of Sewage, in reference to its origin, alteration, and the various circumstances which increase or lessen the possibility of rendering it practically available for fertilizing land.

I shall then bring before you an account of the various suggestions that have been put forward for the purpose of solving this problem and a statement of such data, as may be serviceable for forming an opinion as to their respective merits.

The chief element of the agricultural value of sewage originates from the excrement, solid and liquid, of the population.

The value of these excretions as manure has been sufficiently pointed out by various chemists, and they had long been in use, both in this country and on the Continent, but without any attempt that I can find to manufacture them into a more portable and less objectionable form than that in which they are delivered by nature, until early in this century, when in 1802, a person of the name of Estienne proposed to gather the excrements into tanks, to allow the liquid part to run off, and to dry the residue in the sun, either alone or mixed with lime.

When this dry mass was stowed into sheds in heaps, its temperature rose to 212° F, afterwards it was crushed into a powder which is stated to have been devoid of smell and not very bulky. I may state in confirmation of this that a few years afterwards, Sir Humphry Davy, in a lecture delivered to the Board of Agriculture, mentioned especially mixing quicklime with night-soil to deprive it of its disagreeable smell, and observed, at the same

* Lecture delivered before the Chemical Society, April 6th, 1857.

time, that the Chinese, whom he considered to possess a greater amount of practical knowledge of the use and application of manures than any other nation, are in the habit of mixing their nightsoil with one-third of its weight of fat-marl, making it into cakes, and drying it by exposure to the sun. "These cakes," Sir Humphrey adds, "we are informed by the French missionaries have no disagreeable smell and form a common article of commerce of the empire."

After these suggestions on disinfecting night-soil and depriving it of odour, no further progress appears to have been made until 1835, when Poittevin noticed the value of carbon, as an adjunct to marl, for disinfecting substances, and obtained a patent for the preparation of a powder containing charcoal for this purpose.

This suggestion of M. Poittevin's of using carbonaceous matters for the purpose of depriving substances of any objectionable odour seems to have been followed by a great many persons who obtained patents for various methods of converting excreta and other refuse into manure. The principal differences consist in the methods of obtaining the carbonaceous matter for this purpose; in some cases, carbonaceous residues from other operations were used. The first person after M. Poittevin, who made any step in this direction, appears to have been the Count de Hompesch, in 1841, who proposes to grind up the carbonaceous residue from the retorts after distilling the oils from clay, slate, asphalt, or minerals containing bitumen, and to mix this powder with animal or putrid matters to form a "most powerful manure without any smell." The Count observes, that when iron pyrites are present in the mineral, which would be the case were schist employed, they are to be dissolved out of the powder with an acid, previous to use.

In 1842, Dominic Frick Albert proposed to collect the refuse from nearly every trade and manufacture, and to mix it with animal excretion and charcoal for the purpose of making manure.

In June, 1845, M. de Buisson distilled oils from bituminous matters, and employed the carbonaceous residues from the retort, mixed with the ammoniacal liquor from the distillate, to absorb fresh or coagulated blood or any other soft animal material, such as night-soil or brains; or liquid, such as urine, by which the power of the manure is increased.

In August, 1845, John Evans proposed to manufacture manure by collecting and mixing together every kind of animal refuse with urine, and the refuse of a great many trades. These substances were to be treated, under different circumstances, with different chemical agents, such as decoctions of oak, pyroligneous acid, sulphate of iron, alum, pyrolignite of iron, naphtha mixed with a small quantity of nitric acid, sulphuric acid, and magnesia.

Early in 1847, Mr. Edward Brown proposed to neutralize the odorous and noxious gases emanating from fecal substances, so as

to preserve them for manure, without injury to the public health, by means of "sulphate of iron, chlorides of sodium, iron or manganese, nitrates, sulphates, and chlorides of lead, copper, zinc, and tin; pyroligneous acid, coal-tar, or schistous and bituminous extracts." The fecal substances were to be mixed with an absorbent powder, made by incinerating in close vessels coal, or wood ashes, and earth, street or road sweepings, sawdust, bone-dust, and the waste water of tan-yards, cotton mills, &c.

In May, 1847, Mr. William Bridges Adams, and Mr. Robert Richardson, proposed to construct at railway stations close cisterns of slate or metal or other eligible material, into which the urine might drain, or to use chemicals for absorbing "the volatile alkali and other gases."

Edward Parker, in October, 1847, proposed to submit a mixture of vegetable and mineral materials to the action of fire, and amongst the things suggested, are night-soil and urine.

Mr. James Young, now of Glasgow, in a paper read before the Manchester Literary and Philosophical Society, in December 1847, suggested for deodorizing cesspools, the refuse of the chlorine process, which is principally chloride of manganese, and which he stated was at that time a useless product, one factory throwing away daily thirty-six tons of this solution of about sp. gr. 1.280 or 1.300.

Mr. Jasper Wheeler Rogers, in 1848, proposed to prepare charcoal from peat and combine it with animal excrement, for the purpose of making an inodorous manure.

In 1849, M. Louis Napoleon Legras proposed to construct water-closets in such a manner as to separate and keep apart the solid feces from the liquid. These were afterwards to be deodorized and mixed with charcoal ground to a powder, or with soot.

Mr. Henry James Tarling, in 1850, manufactured manure with night-soil and highly carbonized refuse tan as the disinfecting material.

In June in the same year, Paul D'Angely deodorized every species of excreta by using a fluid "composed of fresh bark, rue, or wild mint, and sulphate of iron;" the fecal material was afterwards to be dried in a chamber and mixed with powdered peat charcoal.

In 1850, James Hamilton Brown disinfected fecal and putrid matters by the addition of basic salts, such as subsulphate of the peroxide of iron. A solid disinfecting agent or one in a state of paste was to be made by mixing "some metallic salts with some cheap oleaginous material." Chloride of calcium neutralized by gas liquor was to be employed likewise, or a lactiform liquid "made by mixing oil with water and some alkali." No carbonaceous matter appears to have been added; but, in case filtration were necessary, preference is given to a filter formed of carbonaceous substances. It is also stated that more rapid and perfect

clarification or decantation may be effected by means of any compound of alumina, but, particularly, "the double sulphate of alumina and potash, or the impure sulphate of alumina."

In 1852 Mr. William Armand Gilbee employed a decomposing powder composed of molasses or the residues thereof, slacked lime, sulphate of iron or zinc and clayish magnesian earth, which was to serve the purpose of converting fecal matters into a manure fit for agricultural purposes.

In 1854, Mr. John Thornton Herapath employed the coke of Boghead coal or Torbane mineral, either before or after the aluminous ingredients are abstracted, for drying, deodorizing, and absorbing urine, feces, &c.

In October of the same year Mr. William White carbonized night-soil or other animal refuse and fish in a close retort, and while in a state of incandescence introduced a quantity of potash or soda, then after closing the mouth of the retort the whole was exposed to a bright red heat for about an hour. A portion of the carbonaceous matter is said then to combine with the nitrogen of the atmosphere which finds its way into the retort, forming cyanogen, and this unites with the base of the alkali employed. The distillate is condensed in a solution of common salt or dilute acid, added to the cyanic compound in the retort, and the whole afterwards mixed with such substances as dried night-soil, superphosphate of lime, common salt, wood-ashes, dried blood, and soot. Disease, attacks of insects, or fungi on plants, are said to be prevented by a mixture of hydrate of lime, sulphate of alumina, sulphate of protoxide of iron, sulphate of magnesia, charcoal prepared as above, biphosphate of lime, and chloride of sodium, together with the condensed volatile matters, and this is termed the "plant preservative."

Mr. Alexander Macdougall, in February, 1856, proposed to subject night-soil and a number of other animal matters to the joint action of heat and sulphurous acid, and in July of the same year, Mr. James Alexander Manning manufactured a manure or fertilizing agent from the waste of towns and other localities by subjecting fecal matters from privies and cesspools, and all animal excrements, stale urine, also the diluted or undiluted urine from public urinals, railway stations, and factories, together with other kinds of refuse, to the action of sulphuric acid or to distillation.

Mr. Bridges Adams has, in a recent number of the "Engineer," discussed the possibility of dealing with the excrement of the population of London without allowing it to pass into the sewers. He considers that if by a mechanical arrangement of water-closets, the feces and urine are collected apart, the latter may be barrelled up and very profitably transported by rail to agricultural districts.

He estimates the annual quantity of urine at 24,428 tons; but

since urine contains 97 per cent. of water and only 1 per cent. phosphoric acid and nitrogenous substance equivalent to only 0·7 per cent. of ammonia, it would be necessary to use about 30 tons for the purpose of applying $\frac{1}{2}$ cwt. of ammonia to an acre. The cost of carriage for this quantity, 20 miles beyond London, would be about £2, whereas $\frac{1}{2}$ cwt. of ammonia can be bought for much less than £2, either as sulphate of ammonia or guano, and the cost of application to the land would be very considerably less than that of urine.

To dispose of the feces, Mr. Adams suggests removal by carts from each house, and considers that it would be no difficult matter to distil them in gas retorts, to use the gas produced for lighting and the residual charcoal as fuel. But Mr. Adams does not offer any suggestion as to means by which (for this purpose) the feces are to be dried and deprived of their water, amounting to more than $\frac{7}{10}$ by weight.

To compensate for the purification by water, Mr. Adams says "in constructing closets without water the arrangement must be such as to separate the fluid from the solid by a diaphragm. To prevent gaseous odour from arising two processes may be used—first, a chemical absorbent, and, secondly, an inch or two of fluid oil floating on the surface, through which both fluid and solid will pass, and be thus hermetically sealed. Probably a gallon of oil at about three shillings would be required once in three months. In a family of twelve persons, the total solid produce in three months would be about three feet. If made to fall into a cast-iron retort built into a furnace, it would take scarcely any trouble, and only a few hours of a night, once in three months, to burn a few coals and utterly destroy it, burning the gas evolved at the same time."

From this account of the various propositions that have been made for the treatment of excremental material so as to render it of value to the farmer, it will be evident that the question has received considerable attention among practical men. With regard to the actual working of any one of these methods, I am not able to furnish any information; but the merits of the respective methods will readily be apparent to the chemist.

I will now request your attention to the actual quantity and value of the manurial substances contained in human excretions.

From a comparison of the results obtained by various observers, Mr. Lawes and Dr. Gilbert have computed that the quantity of fecal and urinary excretions voided daily by a single individual, contains on the average two ounces of dry substance. Of this one-fifth may be taken as equivalent to ammonia, another fifth as mineral substance, and the remaining three-fifths as organic substance. The agricultural value of excremental material is therefore

to be sought in the $\frac{2}{3}$ ths of dry solid, representing ammonia and mineral substances.

For the purpose of calculating the quantity of phosphoric acid in excremental material, I have taken as a basis the analysis of the ash of feces and of urine, published by Mr. Way in the Journal of the Royal Agricultural Society. According to those analyses the average quantity excreted daily by each individual is 30·4 grains.

The quantity of potash calculated from the same analyses amounts to 21·7 grains daily for each individual.

For a population of 10,000, therefore, the quantity of dry solid in the excrement will amount to 205 tons, which would have a money value of £3075 sterling. This estimate is made upon the assumption that the ammonia in excremental material is worth £70 per ton; the phosphoric acid £56 per ton, and the potash £70 per ton.

I call attention to the amount of these three substances particularly, because there is no question as to their agricultural value, provided they are to be procured in an available condition. But in fixing a value upon manure, the relation between its mass and the amount of these valuable ingredients, must be taken into consideration.

In the case of excremental material this circumstance seriously affects its value as manure. Thus, for instance, the quantity of water in fresh feces amounts, according to the analysis of Berzelius and others, to upwards of 70 per cent. while that in urine amounts to 93 per cent.

This constitutes the chief obstacle to the profitable use of excrement for agricultural purposes; for, although the gross amount of valuable substances, contained in the excrement even of a small population may be very considerable, the separation of the large amount of water would be too costly to admit of being practically carried out, and the admixture of absorbent substances would decrease the value per ton, while it augmented the cost of transport.

However, under the system of sewers which is now general in London, and which prevails more or less in most towns throughout this kingdom, the utilization of excremental material in this manner is impossible, on account of the large proportion of water with which it is blended in its passage into the sewers; and the profitable use of night-soil as a manure, either in the natural state or prepared by any of the methods already described, will be restricted to the immediate neighbourhood of those places where water-closets are not in general use.

This brings me to the consideration of the more special subject of this discourse, viz.: the utilization of town-sewage for agricultural purposes.

The chief element of the manurial value of town-sewage is the

excremental material, and this, in the instance of London with a population of 2,600,000, amounts annually to 53,393 tons of dry solid, which, as I have already shown, contains ingredients which give it a value of £15 per ton at least.

| | |
|---|-------------|
| The quantity of ammonia which this contains, or is capable of producing is . . . | 11,440 tons |
| The phosphoric acid . . . | 1,839 „ |
| The potash acid . . . | 1,331 „ |

These three items make up a money value of about £836,834.

In this estimate no account is taken of the suspended particles of animal substance, such as skin, hair, &c., which find their way into the sewers from various sources, and which I have myself found to represent a quantity of ammonia nearly equal to 0·5 per cent. of the dry solid residue obtained by evaporating sewage-water. In addition to these substances I may mention that the quantity of soda (NaO) calculated from the same data, and originating from excreta amounts annually to upwards of 2000 tons.

It may be that materials of agricultural value pass into the sewers of London, even at the present time, from other sources; but as this would not be the case when the sanitary arrangements of the town shall have acquired a normal condition, no notice of such materials can be required for my present purpose.

The circumstances which operate in the opposite direction, viz. reducing the value of the sewage for agricultural purposes, consist chiefly in the admixture of the water consumed for household purposes, for some manufacturing operations, and also the rain falling upon the area drained by the sewers.

The water supply being very unequal in different towns, the sewage will be proportionately different in concentration, and probably also in condition, since the sewage of towns, when there is a copious supply of water, issues from the mouths of the sewers for the most part fresh; while that of towns where the water supply is small, or the construction of the sewers defective, is always putrid, and contains the greater part of the nitrogen in the state of ammoniacal salts.

In all towns in Great Britain which are supplied by water companies, the consumption is in round numbers from 12 to 50 gallons daily for each individual, inclusive of wholesale consumers. The difference arises chiefly from the fact that in many places there are neither water-closets nor sewers. Where the consumption per head is least, closets are used only by a few; and where the consumption is high, closets are almost universal. As instances of the actual quantities of water supplied in different towns I may mention—

| | | |
|-------------------|--------------|---------|
| Ashton-under-Lyne | 14 | gallons |
| Duckinfield | } . 12 to 14 | ,, |
| Bury | | |
| Brighton | . . 20 | ,, |
| Preston | . . 20 | ,, |
| Edinburgh | . . 25 | ,, |
| Liverpool | . . 22 | ,, |
| Manchester | . . 25 | ,, |
| Glasgow | . . 50 | ,, |

In some towns in America the supply reaches as much as 100 gallons per head daily.

In 1854, the water supply of London averaged 20 gallons per head daily; at the present time it amounts to 32 gallons per head daily, the total amount supplied by the metropolitan water companies being 81 million gallons daily; in addition to this 81, about 11 million gallons are obtained daily from the deep wells for brewing and other manufacturing purposes, a considerable amount of which ultimately passes into the sewers. Then there is the rainfall which, on the average, amounts to about 25 gallons per head daily, so that the total quantity of water disposed of in London amounts to 167 millions daily, or 600,955 million gallons yearly.

Consequently the 53,393 tons of excremental substance produced in the year will be distributed throughout a quantity of water which in round numbers may be fixed at 250 million tons, and one ton of excremental substance containing the constituents that have a money value of £15, will be distributed through a mass of liquid weighing 4682 tons. Herein is the great difficulty of dealing with the sewage for agricultural purposes.

The water itself will contain some substances of value as manure.

Nitric acid.

Organic substance.

Alkalies amounting on the average to 0·5 grains KO in the gallon and 1·0 ,, NaO

Among other substances which are consumed in ordinary household economy, and which furnish a constant supply of ingredients to town-sewage, soap may be mentioned as the most important.

In 1851, the average consumption of soap in Great Britain was 7 lbs. for each person annually. This is a much smaller proportion than is consumed in some places. Thus, for instance, in Jersey, the consumption is found to be at the rate of 13 lbs. per head; in the Isle of Man, where the population is less wealthy than in Jersey, the individual consumption is 8½ lbs. In Jamaica it is 5 lbs. The allowance to inmates of workhouses and prisons in this country is about 10 lbs. per head yearly, and assuming this to be no more than necessary, it has been found that after deducting from the

quantity made, the quantity exported, and also the quantity consumed by manufacturers of woollen fabrics, &c., there remained only sufficient to supply 15,790,000 persons at this rate, and it may therefore be concluded that 5,000,000 persons in Great Britain were not in the habit of using this important necessary at all, or else that a larger number did so very sparingly. However, taking 7 lbs. as the average consumption, this would give for London a total of 8705 tons annually. The corresponding quantity of soda would be 609 tons, and that of fat 548½ tons.—No agricultural value can be assigned to either of these ingredients of sewage, but the fact that the quantities are present in it is perhaps worth notice.

The number of methods that have been proposed for obtaining manure from town-sewage are not by any means so numerous as those for working excremental substances. For the present purpose they may be considered under three heads.

1st. Filtration through various media alone, and after the addition of chemical substances.

2nd. Precipitation by means of re-agents.

3rd. Irrigation.

The method of sewage filtration through various media, has been urgently advocated by many. But it will be at once evident to the chemist that the possible result of such an operation cannot be profitable, so far as regards the separation of those ingredients of sewage which constitute its chief manurial value, however advantageous it may be in a merely sanitary point of view.

Even taking the most favourable case, viz.: that the excremental material issues from the sewers undecomposed, the fact that the principal part of the ammonia-generating substances, namely—the urea and uric acid, are soluble, and that, the chief part of the phosphoric acid exists as phosphate of soda or potash, will show that little is to be gained in this way. Moreover the enormous proportion of water which is mixed with the valuable material, amounting in the case of London sewage to upwards of 4000 parts, is much greater than would be sufficient for dissolving even the phosphate of lime; for, according to Professor Bischoff, phosphate of lime is soluble in about 2000 parts of water saturated with carbonic acid, and the existence of carbonic acid in some sewage-water, especially when decomposition has set in, must be very considerable.

A sample of the solid suspended substance of the Croydon sewage was analysed by Mr. Way, and the absolutely dry substance was found to contain only 2.73 per cent. phosphoric acid and nitrogen equivalent to 3.94 per cent. ammonia.

Owing to complaints that have been raised by landed proprietors in the neighbourhood of the river Colne of the contamination of the water by the sewage of the town of Uxbridge, a plan has recently been adopted for filtering the Uxbridge sewage through

peat charcoal, by Mr. Pilbrow the engineer to the Local Board of Works. He uses alternately two filters consisting of troughs 25 feet long, $2\frac{1}{2}$ feet deep, and $2\frac{1}{2}$ wide, through which the water flows as it issues from the sewers and is then discharged into the river. The charcoal remains serviceable for six weeks or thereabouts. The plan is said to purify the water sufficiently to remove objection*; it is inexpensive, and the spent charcoal sells readily at £1 per ton.

In 1851 it was proposed by Mr. Richard Dover to add before filtering the sewage, a mineral acid together with salts, and on account of their economical use, he preferred hydrochloric acid as the acid, and chloride of sodium (common salt) and protosulphate of iron, as the salts to be employed. The filtering medium was principally to be of charcoal or gypsum; but, if little valuable matter for agricultural purposes is retained by the charcoal from filtering ordinary sewage-water through it, still less must result from sewage-water to which acid has been added, by reason of the acid rendering soluble any insoluble phosphate which might be in the fecal matter, in which state I need scarcely add it must inevitably pass through any of the filtering media suggested by Mr. Dover.

Other methods of filtering sewage, both previous to and after treatment with chemical substances, have been proposed; but from the general improbability of any agricultural advantage being gained from such manipulation of sewage, for the ammonia, the potash, and the phosphoric acid salts are all little, if at all, arrested by them, I may pass them over without further remark.

I now come to speak of the treatment of sewage by processes under the second head, namely—*Precipitation by means of various re-agents*. The method which seems to be the most favoured for precipitating the solid material from sewage is the one familiarly known as the “liming process.” I say favoured, because hitherto it has been more adopted than any other. This method consists in adding lime, hydrate of lime, or milk of lime, to the sewage-water. The lime in this case seizes upon some of the organic substances, and forms a kind of network which, in falling to the bottom, carries with it whatever suspended particles there may be in the liquid, leaving the water tolerably clear. Unfortunately, however, this treatment, though efficacious in separating some substances that are dissolved in sewage, has no such action upon the ammoniacal substances, the potash salts, or perhaps to any considerable extent upon the phosphoric acid.

In confirmation of this, I may quote some analyses, in which I have perfect faith, of manures prepared by this method from sewage at different localities.

* This plan has since been abandoned as insufficient.

| Analysis made by | Voelcker. | T.J.Herapath. | Smith & McDougall. | Calvert. |
|-----------------------------|------------|---------------|--------------------|-------------|
| Locality of Sewage. | Leicester. | Cardiff Gaol. | Manchester. | Manchester. |
| Water | 10.52 | 4.71 | | |
| Organic Matter | 12.46 | 15.91 | 22.00 | 24.56 |
| Insoluble Siliceous Matter | 13.50 | 2.74 | | } 9.66 |
| Sulphate of Lime | 1.76 | 3.26 | | |
| Oxides of Iron and Alumina. | 2.89 | | | } 65.16 |
| Manganese | — | — | — | |
| Carbonate of Lime | 52.99 | } 69.28 | | |
| Carbonate of Magnesia | 3.67 | | | |
| Sulphate of Sodium | 0.45 | | | |
| Potash | 0.26 | | | |
| Phosphate of Lime | 2.27 | 4.10 | 1.51 | |
| Phosphoric Acid | — | — | — | 0.62 |
| | 100.77 | 100.00 | — | 100.00 |
| Nitrogen | 0.60 | 1.125 | | |
| = Ammonia | 0.72 | 1.366 | 0.525 | — |

This was one of the earliest processes and arose out of an invention by Dr. Clark, of Aberdeen, patented early in 1841, for “a new mode of rendering certain waters (the water of the Thames being among the number) less impure and less hard for the supply and use of manufactories, villages, towns, and cities.”

Dr. Clark, some time in that year, was engaged at Manchester with Mr. John Graham, in making experiments with his process at Mayfield Print Works, and an experiment was made upon the Mayfield return waters, which were highly colored with madder and soap-liquor. The experiment in removing all colour, &c., being so successful, led Mr. Graham afterwards to adopt it at the works on the large scale. The river Medlock, which receives all the sewage of Manchester was next tried, and the process proving successful upon this likewise, Dr. Clark repeated his experiments and ascertained how much lime it required to purify the Medlock water, of the sewage it contained, and fixed it at about 1 ton per day. Dr. Clark was also in correspondence and had interviews with the authorities of the Duke of Bridgewater's Canal to purify and sweeten the water before it should enter the canal. I may add, that I do not think that Dr. Clark contemplated this action when he took out his Patent for purifying water; yet it would appear that shortly afterwards he accomplished what I have stated.

I may observe, that recently Dr. R. A. Smith, Mr. Macdougall and Mr. Crace Calvert have examined into this process with a

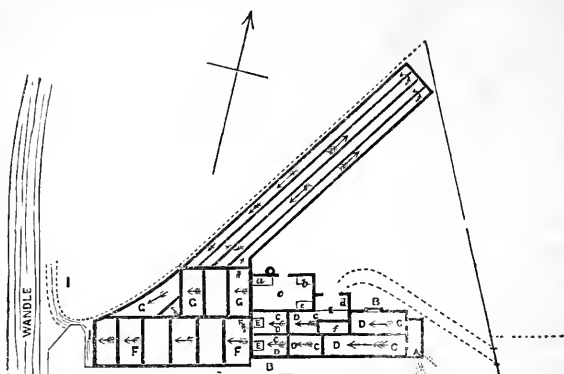
view to its being adopted by the authorities of Manchester and Salford in purifying the river Medlock and the Bridgewater Canal, and I think I may say it has received a general recommendation from those gentlemen as a proper sanitary movement; but they concur in the opinion that the deposit cannot be considered as a valuable manure. The two former gentlemen report that they "found the smell of the Medlock water was not entirely removed by precipitation, or if removed, that it soon returned." They also remark "we can, however, calculate on no receipts from products."

Although Dr. Clark's experiments in 1841 were well-known to many persons at Manchester, I should judge that they were not generally so, from the fact that the use of lime in precipitating sewage has since been the subject of several patents, the earliest of which was taken out by Mr. William Higgs in 1846, in which, along with several mechanical arrangements, he includes hydrate of lime, commonly termed slacked lime, to "precipitate the solid mineral and vegetable matters from sewage." Mr. Higgs pumps the sewage into tanks, where it is limed, and the precipitate subsiding, the water is drawn off. The precipitate removed into shallow canals and exposed to become more dry, is afterwards moulded into bricks which are dried and afterwards broken up into powder. Mr. Higgs has furnished me with an analysis made by himself of the manure so obtained from the sewage-water of Tottenham, but the analysis is not definite enough to put us in possession of the value of the article for agricultural purposes; as for instance, it is stated to contain organic matter, *rich in nitrogen*, 31.60 per cent.; phosphates 8.64 per cent.; sulphates, with alkaline bases, 3.87 per cent.; whereas what is really required is the *nitrogen*, *phosphoric acid*, and the *potash* of the alkaline bases, from which alone can be calculated the real money value of a manure.

In 1851, Mr. Thomas Wickstead proposes to manufacture manure from sewage-waters by mixing them with milk of lime, collecting the deposit, and submitting it to certain centrifugal drying machinery; works have been erected at Leicester upon a large scale to work this process, under the superintendence of Mr. Wickstead. The water is precipitated in tanks; the analyses of the manure I have given before.

I may also state that besides Tottenham and Leicester, the liming process has been tried and adopted at several other places, among others at Croydon, where from its proximity to London, and through the liberality of Mr. Chown, the proprietor of the works, for some months back I have had ample opportunity, from time to time, of examining the workings and the results; and as the method appears simple, and is capable of being adopted in some places with little expense, I think it may not be out of place to give rather a full description of the works.

SEWAGE WORKS AT CROYDON.



The sewage is brought to the works by means of 4 pipes at A. Immediately that it issues from these pipes, slaked lime is added, and well mixed by a wheel driven by a current of the sewage water, it then flows into the building B, in which are two sets of beds C, each 106 feet long, 13 broad, and 2 deep. These are used alternate weeks, one being worked whilst the solid matter is removed from the other. In these beds, more especially the first, a large quantity of the solid matter held in suspension and solution is deposited, and the water from the previous admixture of the lime is rendered innoxious. The cross walls D, for intercepting the solid matter, are built with apertures to about three inches of the level of the water, so that the solid matter precipitated is not again disturbed, and the water flows without any apparent current, and percolating through a bed of stones E, which prevents the possibility of the escape of any paper, or other solid matter, except in a state of fine division. The water then flows through other channels, or reservoirs, F G H, where a large quantity of the lighter solid matter is precipitated, and the water discharged in a tolerably pure state at I K L. The reservoir F is 104 feet long and 23 wide. G is 30 feet in width; the cross walls on these beds are constructed on the same principle as those in the building, and the time occupied by the passage of the water from A to I and K is about $1\frac{1}{2}$ hours. The reservoirs marked H have been recently constructed and on another principle, the walls being perforated only at each alternate end, consequently the water is retained for a much longer period (3 hours being occupied in its passage from A to L), and is discharged in a much purer state than at I and K, proving that the increased transparency of the water is in ratio to the increased area of reservoirs and decreased speed of the current.

The solid matter deposited in the beds C averages about 14 or

16 tons a-week: this is conveyed to the well, and by means of a Jacob's ladder lifted to a lead-lined machine, where by the mixture of other materials, a valuable and remunerative manure is said to be obtained.

In 1852 Mr. Henry Stothert proposed to precipitate "the more substantive parts of sewage water" by a "combination of compound animal and vegetable charcoal" with fresh caustic lime, or sulphate of alumina or sulphate of zinc; the charcoal might be obtained by distilling the precipitated sewage matters or night-soil, &c. Again, in 1854, Mr. Wickstead proposes to use lime and finely divided charcoal; these are to be mixed up with water, and to flow into the sewage in a stream.

The moist precipitate from sewage-water obtained by the liming process has always an unpleasant odour, which, in most cases, is removed by the admixture of a small quantity of charcoal, or some carbonaceous matter, or residue from a process. Whether it was to obviate the necessity of this, after mixing with charcoal to deodorize the sewage precipitate, that these processes were suggested, I cannot say: but some persons have inferred, that as dry charcoal has the power of absorbing and retaining gases and amongst these ammonia, so should it take the ammonia in the sewage-water, and this reasoning may, perhaps, have been the cause of the suggestion; it has, however, been ascertained by actual experiment, that charcoal has no power whatever upon solutions of ammonia or its salts; and no portion of them is retained by filtering through any thickness of charcoal.

A process has recently been tried in Edinburgh, and one or two other towns in Scotland, upon rather a large scale, under the superintendence of Mr. James Alexander Manning; but the whole of the sewage of any one town has not, that I am aware of, been practically worked by it. Mr. Manning, in 1853, proposed to "defecate and separate certain matters from sewage" by employing animal charcoal, alum, and carbonate of soda and gypsum; he found, however, that alum was too expensive, and proposed, in 1854, using the "soft sludge," a refuse from alum-works, instead of the alum. Mr. Manning suggests employing two circular tanks to be used alternately, and capable of holding 100,000 gallons each. Along with this quantity of sewage-water is put 800 lbs "alum sludge," some milk of lime and "waste animal charcoal," the whole agitated for about five minutes, and allowed to subside; when the water is run off, Mr. Manning says the subsidence of the precipitate is so rapid that the mixing and precipitating will all be accomplished in the time it would take to fill the second tank. The same materials are said to serve for three more operations upon the same quantity of water. Mr. Manning has favoured me with the analysis of two distinct operations upon the sewage of Edinburgh, made by Dr. Penny, of Glasgow:

| | | |
|---------------------------|--------|--------|
| Organic matter . . . | 37.43 | 50.00 |
| Phosphates . . . | — | 10.14 |
| Phosphate of Lime . . . | 2.05 | — |
| Chlorides and Sulphates . | 22.89 | — |
| Carbonate of Lime . . . | 1.77 | 1.75 |
| Sulphate of Lime . . . | — | 9.46 |
| Silica . . . | 19.73 | 23.98 |
| Alumina . . . | 16.13 | — |
| Omitted in analysis . . . | — | 4.67 |
| | <hr/> | <hr/> |
| | 100.00 | 100.00 |

| | | |
|---------------|------|------|
| Ammonia . . . | 1.50 | 2.95 |
|---------------|------|------|

The results are given upon the material perfectly dried, which would not be the case in practice, for artificial manures all contain from about 10 to 20 per cent. or even more of uncombined water, which they lose at 212°F. If we take into consideration this water, the first material does not appear to be very distinct from the results obtained with lime upon sewage-water; the second material, however, is considerably different. An extraordinary addition in working the process of "waste animal charcoal," as Mr. Manning terms it, but which is a substance of high money value in the market, might account for the very great increase of phosphates over the first; but the increase of ammonia I cannot account for in any way. In the event of the alum sludge becoming a scarce commodity, Mr. Manning proposes to manufacture it, and thinks he can do so, at a cost not exceeding 5s. per ton exclusive of carriage.

But although I have called attention to the large amount of phosphates and ammonia in the second material furnished by this process, and they are greater than I have hitherto observed in any precipitated sewage, I need scarcely say that they form but a very small item of what passes away in the water from the process.

Before leaving this part of the subject, I would ask you to consider the several processes for treating excreta and sewage, which I have brought before you this evening, and to call your attention to the great similarity which exists between many of them. This may, I think, in a great measure be accounted for from the circumstance that until recently there was a great difficulty in ascertaining what inventions had been made the subject of patents. But now that all the specifications of patents are being printed, together with classified indices, and abridgments of specifications relating to particular subjects, by the Commissioners of Patents, under the superintendence of Mr. Woodcroft, it is to be hoped that in future there will be less needless expenditure of time, money, and labour, by the inventor, and that before he enters

upon a field of discovery, he may study for himself what has already been done by those who have preceded him in the subject he has under contemplation.

I come now to consider the subject of *irrigation*, and shall do so as shortly as possible.

It would be needless to speculate upon the origin of irrigation by water alone. In Egypt, Persia, and China it was long practised before it found its way into the more Western nations, and to us. The earliest notice which I have observed in this country of the value of water for irrigating land, is to be found in the work upon Natural History, written by the great Lord Bacon, nearly two and a half centuries ago. He there observes that there are two ways of accomplishing this; the one is "by letting in and shutting out water at some seasons," and this serves only for meadows which are along some river, and the other is "to bring water from some hanging grounds where there are springs, into the lower grounds." Lord Bacon observes that "it maketh an excellent improvement both for corn and grass, and it is the richer if those hanging grounds be fruitful, because it washeth off some of the fatness of the earth; but, however," he observes, "it profiteth much."

At this time the luxury of water-closets was unknown, and the fecal matter of the population was not carried into sewers, but collected in cesspools, whence it was periodically removed and used for agricultural purposes. The introduction of water-closets, however, quite altered this state of things, and led to a very much greater amount of water being required by each individual, and the formation of sewers to carry it away; generally if a river passed near or through a town, the sewage was carried into it, or if near to the sea it was discharged on the shore. This state of things generally prevails throughout this country at the present time, in most towns; and when sewers were first originated, and for some time afterwards, was universal; but from observing the beneficial effects of water alone in fructifying the land, or receiving perhaps a hint from some of our foreign neighbours, who, I believe are, and were ahead of us in these matters, it was suggested by some of the more intelligent persons of the community, that the sewage-water might be employed beneficially for irrigating land. I do not exactly know when or where it was first tried; but early in this century it was adopted in several places throughout the kingdom, especially in those favourably situated for its distribution, and free from engineering difficulties. Of course the benefits which have arisen in each instance are not equal, and depend much on the absorptive powers of the soil. The quantity of sewage-water which some soils—sandy soils for instance—will absorb, and beneficially too, is beyond calculation great: whereas the quantity which a heavy clay soil will filter is comparatively very small, and hence arises

the difficulty in distributing in this way the sewage of a large town, and it is wrong, without a thorough geological and personal inspection of a country, to declare that the sewage must have a certain area of space for its distribution upon it.

You are aware that around Edinburgh, and many other towns, some of the meadow lands are manured by sewage-water, and yield large crops of grass, often as much as seven crops in the year. The average rent per annum of these meadow-lands round Edinburgh is £20 per acre. I could instance to you many cases where land, comparatively speaking valueless, has been made highly valuable by sewage irrigation; but I will only select one from the number, as being very striking, but too much so to allow it to be considered as a type of the whole.

The sands between Portobello and Leith, near Edinburgh, which were previously waste sand and of *little* value, growing only a few *whins* and rank grass here and there, were irrigated about the year 1819, with sewage-water from Edinburgh. After the first year of that treatment they bore a fair crop of grass, and have since borne four or five crops annually, and bring in a rent of from £13 to £22 per acre. I believe the extent of the lands is about thirty acres, and they were laid out for irrigation at a cost of about £800. Previous to this very remarkable result of the value of sewage-water the lands between Edinburgh and Portobello had been watered in the same manner, and produced great crops; but here an absolutely barren sea-sand was converted into most valuable property.

In concluding this subject, I cannot but remark that, by no process of chemistry at present existing, can we obtain a highly valuable solid manure from town sewage *alone*; and every day the matter gets more and more complicated from the fact, that it is the natural tendency of the population of this and all civilized countries to have an increased supply of water. In New York one hundred gallons per head of population per diem is the present supply. Still I have, I think, demonstrated, and without exaggeration, that the money value of the manuring matter alone in the London sewage is £836,834 annually; and in other towns, according to population, it may be taken as proportionally valuable. I have also given you a statement of the value of irrigation by sewage, which I believe has been successful in nearly every instance in which it has been tried. And I think that if before allowing a valuable article, away from any town, to run to waste, the case were submitted to a combination of engineering, geological, agricultural, and chemical skill, a portion, if not in some instances the whole, might be saved.

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XXVIII.—*On Algodonite, a New Mineral containing Arsenic and Copper.*

BY F. FIELD, F.C.S.

IN a paper published by Dr. Blyth in the "Quarterly Journal of the Chemical Society," vol. i. page 213, he gives a long account of the mineral Condurrite, originally found in the Condurron Mine, Cornwall, and first analysed by Mr. Faraday in the year 1827. This mineral consists of

| | |
|--------------------------|---|
| Water | 8.987 |
| Arsenious acid | 25.944 |
| Copper | 60.498 |
| Sulphur | 3.064 |
| Arsenic | } 1.507 |
| Iron | |
| | <hr style="width: 10%; margin: 5px auto;"/> |
| | 100.000 |

Faraday supposed that the substance was a mechanical mixture, and the examination of other specimens by Blyth, caused him to entertain the same opinion. The formula deduced by Kobell

from the analyses of Faraday is $6\text{CuO}.\text{AsO}_3 + 4\text{HO}$, in which the copper and arsenic bear the following proportions per cent.

| | | |
|---------|---------|-------|
| Copper | | 70.11 |
| Arsenic | | 29.88 |

And from the analyses of nine samples by Blyth, he obtained as a mean,

| | | |
|---------|---------|-------|
| Copper | | 71.15 |
| Arsenic | | 28.84 |

which quantities correspond to an arsenide containing six equivalents of copper to one of arsenic.

Condurrite, then, appears to be an arsenite of copper, $6\text{CuO}.\text{AsO}_3$, which has been derived from the oxidation or weathering, as it is termed, of the arsenide Cu_6As . M. Domeyko has analysed several specimens, both from the provinces of Copiapo and Coquimbo, in Chili, one of which gave :

| | | |
|---------|---------|-------|
| Copper | | 71.64 |
| Arsenic | | 28.36 |

and another :

| | | |
|---------|---------|-------|
| Copper | | 70.70 |
| Arsenic | | 23.29 |
| Sulphur | | 3.87 |
| Iron | | 0.52 |

A specimen of great brilliancy and purity obtained from the Cordilleras of Copiapo, afforded me :

| | | |
|---------|---------|-------|
| Copper | | 71.56 |
| Arsenic | | 28.44 |

and a second from Coquimbo, extracted from a mass weighing several pounds :

| | | |
|---------|---------|-------|
| Copper | | 71.48 |
| Arsenic | | 28.26 |

leaving no doubt that the formula is Cu_6As . There is, however, another compound of these two elements.

In a small vein in the silver mine of Algodones, Coquimbo, there have lately been extracted small lumps of a white metallic substance, supposed by the owners of the mine to be native silver, but which, on examination, proved to contain but little of that metal, and to consist essentially of copper and arsenic. The physical appearance, and much higher specific gravity (6.902), at once led me to infer that the composition was very different from that of the Domeykite Cu_6As , and an analysis was therefore commenced. The mineral was coated with red oxide of copper, Cu_2O , and the matrix consisted of carbonate of lime. On removing the foreign matters from the surface, which was accomplished with difficulty after much filing and scraping, the interior mass presented a brilliant silver-white aspect, with a strong granular fracture, also white, but quickly tarnishing on exposure to the air. The mineral was quite soluble in dilute nitric acid, and gave a precipitate of chloride of silver on the introduction of hydrochloric acid into the solution. After the separation of silver by this means, the following percentages of copper were obtained:

| I. | II. | III. | IV. | V. | Mean. |
|-------|-------|-------|-------|-------|-------|
| 83.24 | 83.12 | 83.40 | 83.36 | 83.41 | 83.30 |

The copper in each case was precipitated from its solution in weak nitric acid by sulphide of hydrogen, and separated from the sulphide of arsenic by sulphide of potassium. The following numbers show the percentage of arsenic:

| I. | II. | III. | IV. | V. | Mean. |
|-------|-------|-------|-------|-------|-------|
| 16.21 | 16.08 | 16.41 | 16.24 | 16.20 | 16.23 |

In three estimations of silver, the following percentages were obtained:

| I. | II. | III. | Mean. |
|------|------|------|-------|
| 0.32 | 0.30 | 0.31 | 0.31 |

We have, therefore, for the composition of this mineral:

| | | |
|---------|---------|-------|
| Copper | | 83.30 |
| Arsenic | | 16.23 |
| Silver | | 0.31 |
| | | <hr/> |
| | | 99.84 |

Now Cu_{12}As (in which the copper is exactly double of that in the specimens formerly examined) contains

| | |
|-------------------|-------|
| Copper | 83.66 |
| Arsenic | 16.34 |

We may therefore conclude that the mineral under consideration is a compound of twelve atoms of copper to one of arsenic, containing besides a small quantity of silver. I have proposed the name *algodonite* for this mineral, from the mine Algodones from which it was first obtained, believing it to be new in mineralogical science. Specimens have been forwarded by me for the acceptance of the Museum of the Chemical Society, to the care of Dr. Hofmann.

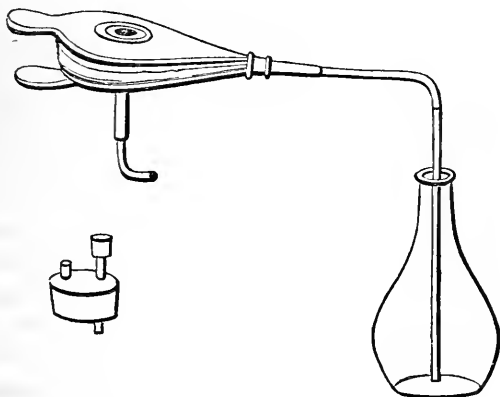
XXIX.—*Volumetric Estimation of Atmospheric Carbonic Acid.*

BY DR. M. PETTENKOFER.

To determine the quantity of carbonic acid in the air, from 3 to $3\frac{1}{2}$ litres of air are generally sufficient. A bottle of white glass is selected, containing about that quantity, and its capacity exactly determined, which is best effected by filling it to the brim with water, and ascertaining the quantity of the water by weight or measurement. The cubic content of the bottle is marked upon it with the diamond, and the number of cubic centimeters thus inscribed on a number of bottles used in a series of determinations, may serve to distinguish them one from the other, inasmuch as, even among a large number of bottles, it will rarely happen that two have exactly the same capacity. Each bottle, before being used in the carbonic acid determinations, must be perfectly clean and dry on the inner surface.

To fill a bottle with the air to be examined, that of a room for example, it is best to use a small pair of bellows, which, instead of drawing in the air directly through the valve, inhales it through a tube of the same diameter as the valve, and attached to it. The mouth of the tube is directed successively to all parts of the space from which the air is to be taken. From the bellows the air is

driven through a glass tube, which must not be too narrow, to the bottom of the bottle, this tube being attached by means of a caoutchouc tube to the nozzle. If the volume of air impelled by one movement of the bellows be approximately known, it is easy to calculate how many times the bellows must be worked, in order to ensure that the air in the bottle is completely replaced by that which is to be examined.



The bottle is then closed by a caoutchouc cap, having two tubular openings for the introduction of tubes. In the chemical laboratories of Germany, these caps are now almost exclusively used instead of perforated corks. One opening of the cap is closed with a round glass rod, and the other with a kind of funnel-tube, which enters the vessel to the depth of about two inches. This upper part of the funnel-tube is a wider tube, which can be closed with a cork.

Thirty cubic centimeters of clear lime-water are next introduced into the bottle through the funnel-tube from a pipette graduated for the purpose; the funnel-tube is closed with a cork, and the other opening of the cap with the glass rod; and observations are made of the temperature of the air and the height of the barometer. The volume of air is equal to the capacity of the bottle *minus* the quantity of lime-water introduced (30 cub. cent. are generally sufficient), and may therefore be easily and exactly reduced to 0° C. and 760 mm.

The bottle is now to be held between the two hands in a nearly horizontal position, and the lime-water moved about in it so as to wet the greater part of the surface. When this agitation has been

continued for eight or ten minutes, we may be pretty sure that the absorption is complete, provided always that the lime-water is in excess.

The next operation is the saturation of the free lime with a known quantity of acid. For this purpose, any dilute acid which is not volatile at ordinary temperatures, may be used. I have hitherto used oxalic acid, the employment of which is attended with only one inconvenience, viz., that it often turns mouldy when kept too long. It is best to make the oxalic acid solution of such a degree of dilution that 1 cubic centimeter of it corresponds to 1 milligram of lime (CaO). This degree of dilution is easily attained by placing a quantity of pure crystallized oxalic acid in the exsiccator over sulphuric acid for a few hours, and then dissolving 2.25 grammes of it in a liter of distilled water at 15°C . To ensure accuracy, the strength of the solution should be tested by precipitating the oxalic acid, and the proper quantity of oxalic acid or of water added, if necessary; but if the proportions just mentioned be carefully observed, no correction will be necessary.

With this solution, the quantity of caustic lime in any given sample of lime-water is easily determined. The lime-water for these determinations is prepared by drenching slaked lime several times with water, and rejecting the first decantations in order to get rid of the alkalies which lime generally contains. The accuracy of the process is not however vitiated by a small quantity of alkali in the lime-water, since the oxalates of potash and soda are neutral, and it makes no difference whether a given quantity of oxalic acid is saturated by lime or by an equivalent quantity of potash or soda. The clear lime-water is best kept in bottles of 300 to 400 cubic centimeters' capacity, and having mouths wide enough to admit a pipette capable of withdrawing 30 cubic centimeters of liquid. These bottles are filled as completely as possible, and well corked.

In making an estimation of carbonic acid, the first thing to be done is to determine the strength of the lime-water which is to be used. For this purpose 30 cubic centimeters of the lime-water are introduced by means of a pipette into a flask, whose capacity is about 100 cub. cent., and the normal solution of oxalic acid added from a Mohr's burette, till a drop of the liquid placed upon turmeric paper no longer turns it brown. The exactness of the method depends mainly upon the nicety with which this neutral point can be ascertained. I have found turmeric paper more

delicate for this purpose than any other reagent, reddened litmus paper, for example. To obtain the greatest amount of delicacy, it is not sufficient to immerse a strip of turmeric paper in the liquid, or to touch it with a glass rod dipped in the liquid; an entire drop of the liquid must be let fall on a rather broad strip of the paper by means of a glass rod or tube. The part of the paper not wetted by the drop then absorbs the liquid rapidly round the whole circumference of the drop, and in this manner the alkaline reaction round the drop is greatly intensified. It often happens, indeed, that a drop of liquid thus let fall on the paper exhibits very distinct brown edges, when a strip of paper immersed in the liquid shows no alkaline reaction whatever. As soon as the brown edge round the drop disappears, the liquid is no longer alkaline. The turmeric paper is so delicate, that the addition of four or six drops of lime-water to the neutralized liquid is sufficient to reproduce the alkaline reaction.

The quantity of oxalic used gives directly the amount of lime in the lime-water, inasmuch as a cubic centimeter of the oxalic acid solution saturates exactly one milligram of lime. Of the lime-water used in my experiments, 30 cubic centimeters required from 34 to 38 cub. cent. of the oxalic acid solution, within which limits the strength of the lime-water prepared as above described will generally fall. In a well corked bottle containing but a small quantity of air, the strength of the lime-water does not vary perceptibly in the course of several days. Even when a bottle holding about 300 cubic centimeters is half empty, samples taken at intervals of 24 hours scarcely exhibit any difference if the bottle is well corked.

Lastly, to find how much lime has been saturated by the carbonic acid contained in the air, the lime-water in the bottle in which it has been shaken up with the air, is neutralised with the solution of oxalic acid. To avoid overstepping the point of neutralisation, small strips of turmeric paper are used, fastened by a small clamp at the end of a stick, which is of such thickness as to pass readily through one of the apertures of the caoutchouc cap, and long enough to reach the bottom of the bottle. As soon as an immersed strip of turmeric paper is no longer distinctly browned, it is necessary, after each addition of acid, to take out a small portion of the liquid with a glass tube, and let a drop of it fall upon the turmeric paper; the remaining portion is then returned to the bottle. The gradual addition of the oxalic acid is continued till the drops no longer exhibit any alkaline reaction. As small

quantities of the lime-water adhere to the sides of the bottle, it is necessary, after each addition of acid, especially towards the end of the operation, to agitate the liquid in the bottle in the same manner as at the beginning of the process, to promote the absorption of the carbonic acid.

If the quantity of carbonic acid in the air is so great that only a small quantity (from 2 to 4 cub. cent.) of oxalic acid is required to saturate the lime, the experiment must be repeated, and about 45 cub. cent. of lime-water, instead of 30, introduced into the bottle at the beginning of the process, in order that at least 10 or 15 milligrams of lime may be left in excess; because an aqueous solution which is but very slightly alkaline, absorbs carbonic acid but slowly, and sometimes imperfectly. In all cases it is advisable to fill two bottles with the same air, and examine the air in both. When once the quantity of oxalic acid required for the first bottle is known, the saturation of the liquid in the second may be performed with greater accuracy.

The method here described is as exact as any others which are in use, and possesses the advantage of being very quickly performed, so that it enables us to determine the amount of carbonic acid in the air at any given time and from any particular part of a given space. The determination of the carbonic acid in the air by weighing, for which a considerable volume of air must be drawn in by an aspirator, and deprived of its water and carbonic acid, gives only the medium quantity of carbonic acid in the air during a considerable interval of time; and, according to my experience, is not well adapted to researches on ventilation in inhabited apartments. But by the method just described, when every thing is well prepared and a proper number of dry bottles and caoutchouc caps are at hand, samples of air may be collected and examined at intervals as short as may be desired. After a little practice, an experiment (not reckoning the time required for the subsequent calculations) may be made in 20 minutes.

It was important to ascertain, whether, when the proportion of carbonic acid in the air is small, a volume of air not exceeding $3\frac{1}{2}$ liters is sufficient to ensure a due degree of accuracy. I therefore made two comparative experiments, in which bottles were used containing 3 and 15 liters. The results obtained with the air of a dwelling-room were as follows:

- (a.) Contents of the bottle 3425 cub. cent.
 Temperature of the air, 18° C.
 Barometer, 718 mm.

The air was shaken up with 30 cub. cent. of lime-water containing 35.7 milligrams of lime.

After the absorption of the carbonic acid, the lime-water still required for its saturation 31 cub. cent. of oxalic acid. Consequently 4.7 milligrams of lime were saturated by CO_2 , which corresponds to 3.7 milligr. CO_2 , or 1.861, cub. cent. CO_2 at 0°C . and 760 mm. Bar.; and on reducing the volume of air in the bottle, after deducting 30 cub. cent. for the lime-water, to the normal pressure and temperature, the amount of carbonic acid in the air is found to be 0.061 per cent.

(b.) Capacity of bottle, 15115 cub. cent. Temperature, height of barometer, and strength of lime-water the same as in experiment *a*. Into the bottle were introduced 130 cub. cent. of lime-water containing 154.7 milligr. of lime. After absorption of carbonic acid, 133 cub. cent. of the oxalic acid solution were required to saturate the lime, so that 21.7 milligr. of lime had been saturated by the carbonic acid. This gives 17.1 milligr. or 8.601 cub. cent. of CO_2 at 0° and 760 mm. Hence the quantity of carbonic acid in the air was 0.064 per cent.

Hence it appears that a volume of air not exceeding 3 liters is sufficient to determine by this method the amount of carbonic acid in the air, with all the exactness that can be required.

Finally, I will observe that this method of estimating the carbonic acid in the air presupposes the same condition as all other methods given for the purpose, viz., that the air contains no other acid than carbonic acid.

XXX.—*On some Constituents of Rhubarb.*

BY WARREN DE LA RUE, PH.D., F.R.S., TREAS. C.S., AND
HUGO MÜLLER, PH.D.

I. INVESTIGATION OF A DEPOSIT FOUND IN TINCTURE OF
RHUBARB.

It has been often observed that when freshly prepared tincture of rhubarb is left to itself for some time, it becomes turbid, and deposits a dark-coloured precipitate, which cannot be redissolved, either by heating the tincture or by diluting it with fresh alcohol. The attention of the Society was recently called to this circumstance by Mr. Whipple, who frequently has occasion to prepare the tincture of rhubarb on a large scale: Mr. Whipple, at the same time, gave an account of a few experiments he had made with the precipitate, and stated that his leisure did not permit of his investigating the subject further, but that he would furnish material to any member who might feel inclined to pursue the inquiry. As it appeared to be very probable that the deposit from the *tinctura rhei* contained some constituents of interest, we availed ourselves of Mr. Whipple's offer; and we take this opportunity to express to him our thanks for the liberal supply of material which he kindly placed at our disposal.

The deposit from rhubarb tincture is of a dark colour, and resinous nature; it resembles logwood extract coarsely powdered, and has in a slight degree the characteristic odour of rhubarb. When heated in a test-tube, it does not melt, but gives off yellow fumes, which condense to a yellow liquid, a black residue being left. Heated on platinum foil, it burns without melting, leaving a tolerably large quantity of ash, which consists principally of potash and lime. Boiled with water, it imparts a yellowish tint to it; but an almost inappreciable quantity of it is dissolved: alcohol, when boiled with the precipitate, assumes a dark yellow-brown tint, but the quantity dissolved is, nevertheless, very small. Similar results are obtained on treating the precipitate with ether, chloroform, and glacial acetic acid. Ammonia, and concentrated sulphuric acid dissolve the greater part, but not the whole of the

substance; the fixed alkalies, on the other hand, when aided by heat, completely dissolve it, with the exception of a slight residue, consisting of accidental impurities; the solution in ammonia, the alkalies, or sulphuric acid, is of a dark, dingy purple colour.

After having determined the leading properties of the deposit by the above-named experiments, its composition was investigated in the following manner:—A considerable quantity of the substance was pulverised as finely as possible and treated repeatedly with boiling spirit of wine (of 86 per cent.) until it no longer dissolved anything; the insoluble residue, which constituted by far the greater bulk of the deposit will be treated of hereafter. The dark yellow solution was filtered while hot, and concentrated by partially distilling off the alcohol; the concentrated solution, on cooling, deposited a flocculent matter of yellow colour. This deposit, after being several times dissolved in alcohol, and allowed to deposit therefrom, became crystalline, and exhibited all the properties of *chrysophane*.

In accordance with the method adopted by Schlossberger and Döpping,* in their analysis of rhubarb, the mother-liquor of the chrysophane was mixed with about an equal volume of ether, when a bulky brown precipitate was formed. This was allowed to stand for a while, and the clear supernatant liquor tested with a fresh portion of ether, in order to ascertain whether any more precipitate could be thrown down. After the precipitation was ascertained to be complete, the deposit was separated by filtration, and set aside. The filtrate was concentrated by distilling off the greater part of the ether, and was then allowed to evaporate spontaneously to dryness. The dry residue was again dissolved in alcohol, and the solution treated with ether, which again caused a precipitation; the filtered solution was then concentrated, and allowed to evaporate to dryness; and these operations were repeated as long as ether caused any precipitate in the alcoholic solution. Lastly, by evaporating the alcoholic solution to dryness, we obtained a small quantity of a substance which did not show any signs of crystallization; it had a brown resin-like appearance, and when powdered became yellow; it dissolved readily, with a turmeric tint, in alcohol, ether, and benzol, and gave a deep red solution with ammonia and the fixed alkalies, and exhibited the other characteristic properties of *Erythroretin*.

The brown deposit separated by ether from the solution of

* Ann. Ch. Pharm., 1. 219.

erythroretin, after repeated solution in alcohol and precipitation with ether, resembles in all its properties the *Phæoretin* of Schlossberger and Döpping.

It will be recollected that we stated that the greater part of the deposit from the tincture of rhubarb, when treated with alcohol to remove chrysophane, erythroretin, and phæoretin, remained undissolved; by digesting this residue with a moderately strong solution of caustic potash, it dissolved completely, giving a dark brownish-red solution. To the alkaline solution hydrochloric acid was added; this caused the separation of a deep brown precipitate, which was first washed with water, then with alcohol, to remove a portion of phæoretin which it still contained. After drying, the precipitate formed an almost black resinous substance, nearly insoluble in alcohol, ether, chloroform, and benzol, but dissolving readily in the alkalis. When heated on a platinum foil, it takes fire without melting. These properties accord with those of the *Aporetin* of Schlossberger and Döpping.

These experiments tend to show that the deposit which forms in the tincture of rhubarb is composed chiefly of:

Chrysophane,
Erythroretin,
Phæoretin,
Aporetin,

the chief constituents being the last named. The chrysophane amounts to about 4 per cent., and hence the rhubarb-tincture deposit is a valuable material for its preparation.

II. PREPARATION OF CHRYSOPHANE.

The investigations of the deposit of the "*Tinctura Rhei*" afforded us an opportunity of studying the properties of chrysophane in connexion with the other constituents of the rhubarb root, and enabled us to devise a method for the preparation of chrysophane, which completely removes the difficulties hitherto experienced in the extraction of that substance from rhubarb. Having observed that chrysophane is only slightly soluble in alcohol, but that it dissolves readily in glacial acetic acid, amyl alcohol, oil of turpentine, coal naphtha, and especially in benzol, and in the lighter oils obtained from Burmese naphtha, to the exclusion of the greater part of the other constituents, it became apparent that the latter solvents might be used with great advantage in its preparation. A few preliminary experiments led to the selection of

benzol,* or the light oils of Burmese naphtha and of amyl-alcohol, as the best suited for the purpose. The deposit of the "Tinctura Rhei" parts readily with its chrysophane when treated in a finely powdered state with benzol (purified coal-tar naphtha may be substituted), in a Mohr's extraction apparatus. In order to prepare chrysophane from rhubarb itself, a preliminary operation is necessary; the crushed root must be previously macerated with cold water, which removes more than 50 per cent. of soluble matter; these not only unnecessarily increase the bulk of material to be operated on, but they also render the extraction of the chrysophane much more difficult. After maceration with water, the root is dried and treated with benzol in a Mohr's apparatus. By operating in the manner described, a very concentrated solution of chrysophane is obtained, and a comparatively small quantity of the solvent is employed.

The fact that chrysophane is but slightly soluble in alcohol, and much less so in the dilute alcohol employed in the preparation of the tincture of rhubarb, led to the conjecture that the greater part of the chrysophane remains in the residuary root. An experiment carried out with such residuary rhubarb as is thrown away in pharmaceutical laboratories, proved this conjecture to be well founded, as the residue furnished 2.6 per cent. of chrysophane. It is, indeed, better suited for treatment with benzol than the original root, in consequence of its not being necessary to macerate it previously with water.

The benzoic solution obtained from either of the above-named sources is concentrated by distilling off the greater part of the benzol; on cooling, the solution becomes nearly solid by depositing the crude chrysophane. The mother-liquor contains erythroretin, and a neutral fat, and it is advisable to sacrifice the small quantity of chrysophane retained in the mother-liquor, by at once pressing the crude chrysophane between blotting paper.

On redissolving the crude chrysophane in hot benzol, a reddish-yellow, and much less soluble body is left undissolved, and the

* Benzol, and the light hydrocarbons obtained from Burmese naphtha appear to be susceptible of a very general application in experimental research, as they are of great value in separating certain classes of bodies from others of a different nature. As examples of this application, we may state that benzoic acid can be readily separated from gum benzoin by means of benzol; guaiacic acid can also be separated by its means from gum guaiacum, the benzol dissolving the acids and leaving the gum unacted upon; on evaporation, the acids are obtained at once in remarkably fine crystals.

hot solution, on slightly cooling, deposits a still further quantity of it in the state of a light flocculent precipitate. The chrysophane is obtained by crystallization, after filtering off the flocculent matter, and concentration of the solution. In order to obtain the chrysophane quite pure, the operation must be repeated several times. The flocculent precipitate proved to be a new body, which appears to have escaped the notice of previous investigators of rhubarb.

In the final purification of chrysophane, both amyl-alcohol and glacial acetic acid offer advantages over benzol; for although it is possible to obtain that substance in beautiful crystals from a benzoic solution, yet the difficulties are less when either amyl alcohol or acetic acid is employed, in consequence of temperature affecting the solvent powers of these latter agents to a greater extent than those of benzol. Although alcohol is not adapted for the extraction of chrysophane, it may be nevertheless used in the final crystallization with advantage.

Pure chrysophane, when crystallized from benzol under favourable circumstances, forms six-sided plates (monoclinic prisms), which bear great resemblance to iodide of lead; the colour varies from a pale yellow to a deep orange, according to the size of the crystals. From alcohol, amyl-alcohol, and glacial acetic acid, it usually crystallises in moss-like aggregations of foliated crystals. It dissolves in 224 parts of boiling alcohol of 86 per cent, and in 1125 parts of alcohol at 30°C. (86°F.). When pure it melts, without decomposition, at 162°C. (323.6°F.), and solidifies on cooling to a crystalline mass.

Although chrysophane dissolves in alkalies, forming definite compounds, its acid properties are very feeble, for it not only does not drive off carbonic acid from its combinations, but even parts with ammonia, when the ammonia compound is evaporated.

It is well known that when chrysophane is dissolved in caustic potash of moderate strength, a beautiful purple compound is formed, the greater part of which remains in solution, but a portion of it gradually deposits as a flocculent precipitate. We have observed that if grape-sugar be added to the compound containing an excess of alkali, and the mixture kept for some hours in a well stoppered bottle, the purple colour gradually disappears, and the solution becomes of a brownish-yellow tint, this phenomenon being accompanied by the disappearance of the

flocculent precipitate. The solution, however, recovers its original purple colour when exposed in a shallow vessel to the air for a few minutes, and the flocculent precipitate is again formed.

Hydrate of potash, at its fusion-point, does not alter chrysophane at first; but if the temperature be raised or the action continued for some time, it first becomes blue, and is then decomposed, at the same time an odour resembling that of caprylic alcohol is emitted. Potassium-alcohol apparently does not destroy chrysophane; it gives rise to a purple compound and formation of alcohol.

Neither chlorine, bromine, nor nitric acid, destroys the yellow colour of chrysophane, but they undoubtedly alter its composition. Nitromuriatic acid, when boiled for some time with chrysophane, forms a liquid body which does not become crystalline on cooling; but it still retains the property of striking a red colour with caustic alkalies. A mixture of hydrochloric acid and chlorate of potash behaves in a somewhat similar manner. If chrysophane be dissolved in strong sulphuric acid, and peroxide of manganese be then added, the red colour disappears in consequence of the destruction of the chrysophane.

0·1426 gramme of chrysophane gave on combustion :—

0·3595 gramme of carbonic acid = 68·76 per cent. carbon.

0·0545 gramme of water = 4·25 „ hydrogen.

If these numbers be compared with those obtained by Rochleder and Held, who analyzed the substance obtained from the lichen *Parmelia parietina*, and by Schlossberger and Döpping, who analyzed the chrysophane of rhubarb, there will be found a perfect accordance in the results, as will be seen from the following table:—

| | Rochleder & Held. | | Schlossberger & Döpping. | De La Rue & Müller. |
|----------|-------------------|-------|-----------------------------|------------------------|
| | I. | II. | | |
| Carbon | 68·45 | 68·65 | 68·69 | 68·76 |
| Hydrogen | 4·56 | 4·59 | 4·24 | 4·25 |
| Oxygen | 26·99 | 26·76 | 27·07 | 27·09 |

Before concluding these observations respecting chrysophane, we are desirous of calling attention to the remarkable resemblance existing between the properties of that body and pipitzahoëinic acid prepared from a Mexican root called *raiz del pipitzahuac*, and described by Weld;* but the analysis differs too much to admit of the two bodies being considered identical.

* Ann. Ch. Pharm. xcv. 188.

Weldo obtained the following numbers:—

| | | | I. | II. |
|----------|----|----|-------|-------|
| Carbon | .. | .. | 72.58 | 73.24 |
| Hydrogen | .. | .. | 8.06 | 8.27 |

From the foregoing numbers Weld derives the formula $C_{30}H_{20}O_6$
 Rochleder and Heldt's formula for chrysophane is $C_{20}H_8O_6$

making a difference in the composition of the bodies of $C_{10}H_{12}$

We cannot refrain from pointing out the possibility of these two bodies being homologues, and differing by $5(C_2H_2)$; this would make the formula of pipitzahoëinic acid to be $C_{30}H_{18}O_6$, which requires 73.17 carbon and 7.31 hydrogen.

III. EMODIN.

In the description of the preparation of chrysophane, it was mentioned that on treating the crude chrysophane with benzol, there is left undissolved a yellowish red residue, and that a further quantity taken up by the hot benzol is deposited as the benzolic solution of the chrysophane becomes somewhat cooled. Although the insolubility of this body in benzol led to its detection, the complete separation of it from chrysophane is attended with many difficulties on account of the latter substance modifying to a considerable extent the properties of the new body.

The best mode of separating the new body from chrysophane is to dissolve the precipitate entirely in hot benzol, and to allow the benzolic solution to cool slowly; the deposit which forms is then separated by filtration, and dissolved by heat in glacial acetic acid, from which it is obtained, in a state of considerable purity and in beautiful crystals as the solution cools. This treatment with acetic acid appears to be essential on account of its removing some foreign matter, the presence of which interferes with the crystallization.

After purification in the foregoing manner, the new body may be dissolved in boiling alcohol, from which it separates on cooling in splendid prismatic crystals, sometimes two inches long, associated in concentric aggregations.

This substance, for which for the present we propose the name

of *Emodin*, is of a bright deep orange colour; in thick crystals it assumes almost a red tint. The crystals are monoclinic prisms, extremely brittle, and resembling isatin in appearance.

Emodin does not melt at a temperature below 250°C. (482°F.), while chrysophane melts at 162°C. ($323\cdot6\text{ F.}$); during the fusion, a small portion volatilizes undecomposed, giving a yellow vapour which first condenses to a yellow liquid, and subsequently solidifies to a crystalline mass.

In its chemical properties, emodin closely resembles chrysophane, the different behaviour to some solvents being the principal distinction between them. Emodin is much more soluble than chrysophane in alcohol, glacial acetic acid, and amylic alcohol. In benzol, however, emodin is much less soluble than chrysophane; hence the value of the solvent in the separation of the two bodies.

Caustic alkalis dissolve emodin with the same phenomena as occur in the solution of chrysophane, and ammonia behaves to it as it does to the latter substance, giving a purple liquid, and flying off completely on evaporation of the solution.

On combustion, emodin gave the following numbers:—

I. 0.165 gramme substance gave:

0.4035 ,, Carbonic acid = 66.69 Carbon
0.0605 ,, Water = 4.07 Hydrogen.

II. 0.1688 gramme substance gave:

0.4120 ,, Carbonic acid = 66.57 Carbon.
0.0603 ,, Water = 4.13 Hydrogen.

The purely empirical formula $\text{C}_{40}\text{H}_{15}\text{O}_{13}$ agrees well with the foregoing analysis, as will be seen from the following table:—

| Theory. | | | | Experiment. | | Mean. |
|-----------------------|---|-----|---|-------------|-------|--------------|
| | | | | I. | II. | |
| C ₄₀ | — | 240 | — | 66.85 | 66.69 | 66.57 |
| H ₁₅ | — | 15 | — | 4.18 | 4.07 | 4.13 |
| O ₁₃ | — | 104 | — | 28.97 | .. | .. |
| <hr/> 359 100.00 | | | | | | <hr/> 100.00 |

Up to the present time, we have not been able to determine any rational formula for emodin.

IV. ACTION OF NITRIC ACID ON APORETIN.

When crude aporetin (that which we used for these experiments, contained phæoretin,) is brought in contact with concentrated nitric acid, a red-brown solution is formed which generates heat, and, evolving nitrous fumes, undergoes further decomposition; if, after the evolution of nitrous fumes has somewhat ceased, the action be assisted by heat, taking care that an excess of nitric acid is present, it will be observed, after boiling the mixture for several hours, that a yellow substance deposits, and that a further quantity may be obtained on the addition of water to the solution after it has become cold. This yellow body is a nitro-compound of acid properties, and is the principal product of the action of nitric acid on aporetin.

The mother-liquor is of a dark yellow colour, and gives, on evaporation, (which is facilitated by adding, from time to time, small quantities of alcohol in order to carry off the nitric acid,) a considerable quantity of oxalic acid coloured yellow with extraneous matter.

The liquor from which the oxalic acid has been separated, gives with alkalies, brownish red tints, in consequence of the formation of salts with an acid still to be examined.

No picric or styphnic acid could be detected among the products of the action of nitric acid on aporetin.

If the yellow nitro-compound is washed on a filter with water, the latter acquires, after some time, an amaranth-red colour; if the washing be continued with considerable quantities of water, it still continues to acquire a deep red colour without diminishing materially the bulk of the nitro-compound.

Boiling water and boiling alcohol dissolve the nitro-compound, and acquire a red colour, but the nitro-compound separates, on the cooling of these solutions, as a yellow powder. Alkaline solutions, when dilute, produce, with the nitro-compound, red solutions, but, when concentrated, a flocculent brown compound deposit, and the solutions become also brown in consequence of their decomposition..

Concentrated ammonia, at ordinary temperatures, forms a beautiful violet compound, part of which precipitates; when dry, it has a bronze lustre. The ammonia compound is soluble in water with a violet colour; acids do not precipitate the original yellow nitro-compound from this solution (as is the case when a very dilute

solution of ammonia is taken), but a violet compound which is soluble in an excess of acid with a red colour.

With a cold concentrated solution of carbonate of potash, the nitro-compound forms a reddish brown crystalline powder which dries with a metallic lustre; it is not very soluble in cold water, but dissolves much more readily in hot water with a purple colour. A hot solution of carbonate of potash acts like a solution of caustic alkali, producing instantaneously, with decomposition, a flocculent brown body.

The solution of the nitro-compound in ammonia changes its colour upon the addition of sulphuret of ammonium to purple and then soon to a dark indigo blue. If an acid be now added to this blue solution, a dark purple precipitate is the result; the precipitate settles readily, and when washed with cold water and dried, resembles indigo. Water dissolves this blue body very sparingly, with a purple colour; the alkalies dissolve it, giving a splendid blue solution. The blue compound is also formed when the solution of the nitro-compound in alcohol, to which has been added a small quantity of hydrochloric acid, is brought in contact with metallic zinc.

The dry nitro-compound, if slowly heated on platinum foil, gives off yellow fumes, leaving a carbonaceous residue; if quickly heated, it deflagrates, but the combustion in this case is also incomplete.

The behaviour of the nitro-compound produced by the action of nitric acid on aporetin, tends to prove that it is identical with chrysammic acid, which is so well characterized by its potash salt, by its transformation into chrysamminamid, and especially by the formation of that beautiful blue compound hydro-chrysamid.

The formation of chrysammic acid from aporetin is of some interest, inasmuch as it has hitherto only been obtained from aloes; it is therefore our intention to completely establish the identity of this acid as prepared from aporetin with that resulting from the action of nitric acid on aloes, by analyzing our substances as soon as we have a sufficient amount of material at command.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

Anniversary Meeting, March 31, 1857.

Dr. Miller, President, in the Chair.

Two Scrutators having been appointed, the Meeting proceeded to the election of Council and Officers for the ensuing year, and the following were declared to have been duly elected :—

President.

Lyon Playfair, Ph.D., C.B., F.R.S.

Vice-Presidents,

Who have filled the office of President.

W. T. Brande, F.R.S.

Thomas Graham, F.R.S.

C. G. B. Daubeny, M.D., F.R.S. W. A. Miller, M.D., F.R.S.

Colonel Philip Yorke, F.R.S.

Vice-Presidents.

B. C. Brodie, F.R.S.

John Stenhouse, LL.D., F.R.S.

Warren De la Rue, Ph.D., F.R.S. A. W. Williamson, Ph.D., F.R.S.

Treasurer.

Robert Porrett, F.R.S.

Secretaries.

Theophilus Redwood, Ph.D.

William Odling, M.B.

Foreign Secretary.

A. W. Hofmann, Ph.D., LL.D., F.R.S.

Other Members of Council.

F. A. Abel.

H. Bence Jones, M.D., F.R.S.

C. L. Bloxam.

G. D. Longstaff, M.D.

G. B. Buckton, F.R.S.

Henry M. Noad, Ph.D., F.R.S.

J. H. Gilbert, Ph.D.

Hugh Lee Pattinson, F.R.S.

W. C. Henry, M.D., F.R.S.

Alfred Smee, F.R.S.

Charles Heisch.

J. A. Voelcker, Ph.D.

The thanks of the Meeting were voted to the President, Officers, and Council, for their services during the past year.

April 6, 1857.

Dr. LYON PLAYFAIR, President, in the Chair.

J. Vernon Heath, Esq., was elected a Fellow of the Society.

A discourse was delivered,

"On the Applications of Sewage to Agriculture:" by Dugald Campbell, Esq.

April 20, 1857.

At an Extraordinary Meeting, held pursuant to notice,

Dr. LYON PLAYFAIR, President, in the Chair,

A Minute of the Council was read, announcing that Mr. Porrett, in consequence of declining health and strength, had resigned his appointment of Treasurer to the Society.

It was moved by Professor Miller, seconded by Dr. H. Bence Jones, and resolved,

That this Meeting deeply regrets that the declining health of Robert Porrett, Esq., has necessitated his resignation of the office of Treasurer to the Chemical Society, and that the thanks of the Meeting be presented to him for the zeal he has manifested in the performance of the duties of that office, for a period of fourteen years.

The Meeting proceeded to elect a new Treasurer by ballot, and the President announced that Warren De la Rue, Ph.D., F.R.S., was duly elected Treasurer of the Chemical Society.

The Meeting then proceeded to elect a Vice-President, in the place of Dr. Warren De la Rue, and the President announced that Robert Porrett, Esq., F.R.S., was duly elected a Vice-President of the Chemical Society.

The Meeting was then resolved into an Ordinary Meeting.

Dr. LYON PLAYFAIR, President, in the Chair.

A resolution of the Council, recommending the removal of the names of fifteen Fellows, whose subscriptions had fallen into

arrear, having been read for the third time, was submitted to the ballot, and duly affirmed by the Meeting.

The following papers were read:—

“On a New Base obtained from the Juice of Flesh:” by Professor Strecker.

“On the Juice of Beef:” by Professor Bloxam.

“On a New Method of Testing Urine:” by Mr. John Horsley.

“On the Fatty Matters of Human Excrement in Disease:” by Dr. Marcet.

May 4, 1857.

THOMAS GRAHAM, Esq., Vice-President, in the Chair.

Dr. Anderson delivered a discourse “On the Alkaline Products of the destructive distillation of Animal Matter.”

May 18, 1857.

An Extraordinary Meeting was held pursuant to notice,

Dr. LYON PLAYFAIR, President, in the Chair.

A Minute of the Council Meeting of May 4, 1857, directing that an Extraordinary Meeting of the Society be convened, to consider the propriety of altering the 11th By-law, so as to admit of the Ordinary Meetings of the Society being held on Thursdays instead of Mondays, having been read by the Secretary,

It was moved and seconded,

That the first and second sentences of the 11th By-law be expunged, and that the following sentences be substituted:

“The ordinary Meetings of the Society shall be held twice in every month, from November to June inclusive, except in the month of January, when the Society shall meet once only. The specific days and hour of meeting to be determined by the Council.”

To this an amendment was moved and seconded,

“That the Meetings of the Chemical Society be held on Mondays, in accordance with its original By-law XI.”

The amendment having been put to the Meeting, was negatived, and the original motion was carried.

The Meeting was then resolved into an Ordinary Meeting.

Dr. LYON PLAYFAIR, President, in the Chair.

M. Auguste Cahours, of Paris, and Professor C. G. Lehmann, of Jena, were elected Foreign Members.

The following Gentlemen were elected Fellows of the Society :—

Edward Thomas Kensington, Esq., Dartmouth.
Frederick Versmann, Esq., Royal Mint.
W. J. Powell, Esq., University College.
T. Williams, Esq., Midland Institute, Birmingham.
George Robertson, Esq., London Docks, Shadwell.
Thomas Coomber, Esq., 7, Unity Street, Bristol.
T. Leech, Esq., Stoke-upon-Trent.
J. C. Buckmaster, Esq., Wandsworth.

The following papers were read :—

“On some products of the Oxidation of Chinese Wax :” by G. B. Buckton.

“On the Chemical Changes which Pig-Iron undergoes during its conversion into Wrought Iron :” by Messrs. F. C. Calvert and C. Johnson.

June 4, 1857.

Dr. LYON PLAYFAIR, President, in the Chair.

The following donations were announced :—

The Pharmaceutical Journal.
The Journal of the Franklin Institute.
The Literary Gazette.
The Journal of the Society of Arts.

W. T. Butcher, Esq., of Wolverhampton, was elected a Fellow of the Society.

Professor Miller delivered a discourse “On the recent progress of Electro-Chemistry.”

June 18, 1857.

Dr. LYON PLAYFAIR, President, in the Chair.

Henry William Field, Esq., of the Royal Mint, was elected a Fellow of the Society.

The following papers were read :—

“On a New Series of Organo-thionic Acids :” by J. T. Hobson, Esq.

“On a New Maximum and Minimum Thermometer, &c. :” by the Rev. J. G. Macvicar.

“On a delicate Optical Test for Didymium :” by Dr. J. H. Gladstone.

“Contributions towards the History of Thialdine :” by Dr. Hofmann.

“On the State of the Air in Ventilated and Unventilated Apartments :” by Drs. Roscoe and Pettenkofer.

“Miscellaneous Observations :” by Dr. Hofmann.

“Analysis of the Water of Tonbridge Wells :” by J. Thomson, Esq.

“Remarks on the Action of Heat on Gold, and its Alloy with Copper :” by James Napier, Esq.

“On the Separation of Chlorine, Bromine, and Iodine :” by F. Field, Esq.

“Analysis of several Minerals :” by F. Field, Esq.

“Action of Sulphuric Acid upon Anisic Acid :” by Louis Zervas, Esq.

November 5, 1857.

Dr. LYON PLAYFAIR, President, in the Chair.

The following donations were announced :—

“Daubeny’s Lectures on Roman husbandry :” from the Author.

“A Compendium of Qualitative Analysis :” by Dr. Griffin, from the Author.

“Magnetical and Meteorological Observations at the Toronto Observatory :”

- “ Smithsonian Report for 1855 :”
- “ Researches on the Ammonia-cobalt bases :”
from the Smithsonian Institute.
- “ On the Bitumen and Petroleum of Trinidad :” by the Earl of Dundonald, from the Author.
- “ On the relation of Gold to Light :” by Professor Faraday, from the Author.
- “ Proceedings of the American Philosophical Society :” from the Society.
- “ The Quarterly Journal of Dental Science :” from the Editor.
- “ The Pharmaceutical Journal :” from the Editor.
- “ Bulletin de la Classe Physico-Mathématique de l'Académie des Sciences de St. Pétersbourg.”
- “ Compte Rendu de l'Académie des Sciences de St. Pétersbourg :”
from the Academy of Sciences of St. Petersburg.

The following papers were read :

- “ On some constituents of Rhubarb :” by Dr. Warren De la Rue and Dr. Hugo Müller.
- “ On the Volumetrical Determination of Atmospheric Carbonic Acid :” by Professor Pettenkofer.

November 19, 1857.

Dr. LYON PLAYFAIR, President, in the Chair.

The following donations were announced :—

- “ Manuscript Copy of Dr. Hope's Lectures :” from Mr. S. Middleton.
- “ Catalogue of the Royal Institution Library.”
- “ Notices of the Meetings of the Royal Institution ” from the Royal Institution.
- “ Proceedings of the Royal Society of Edinburgh :” from the Society.
- “ Proceedings of the Philadelphia Academy of Natural Sciences :” from the Academy.
- “ The Canadian Journal :” from the Canadian Institute.
- “ The Smithsonian Contributions to Knowledge.”
- “ The Smithsonian Report for 1856 :”
from the Smithsonian Institute.

"Transactions of the Wisconsin State Agricultural Society:" from the Society.

Richard Reynolds, Esq. of Leeds, was elected a Fellow of the Society.

Professor Rogers communicated the results of some experiments on Atmospheric Ozone.

A paper was read:—

"On a new Calotype process:" by Mr. J. Mercer.

Professor Williamson communicated a note on a peculiar reaction of Cobalt and Manganese.

December 3, 1857.

Dr. LYON PLAYFAIR, President, in the Chair.

The following donations were announced:—

"The Journal of the Photographic Society:" from the Society.

"The Pharmaceutical Journal:" from the Editor.

"Memoirs of the Literary and Philosophical Society of Manchester:"

"Dalton's new system of Chemical Philosophy:"

"Dalton's Meteorology:"

"Dalton on Microcosmic Salt:"

from the Manchester Literary and Philosophical Society.

"Memoirs of the Academy of Sciences of Madrid:" from the Academy.

"Henry H. Watson, Esq. The Folds, Bolton le Moors, and William Crooks, Esq., 15, Stanley Street, Brompton, were elected Fellows of the Society.

The following papers were read:—

"On Rosolic Acid:" by Dr. Hugo Müller.

"On the Arsenites of Baryta, Lime, and Magnesia, and the separation of Arsenic from other elements:" by Frederick Field, Esq.

December 17, 1857.

Thomas Graham, Esq. Vice-President, in the Chair.

The following Gentlemen were elected Fellows of the Society :—

T. B. Groves, Esq., Weymouth.

W. M. Hindmarsh, Esq., 7, King's Bench Walk, Temple.

John Dale, Esq., Cornbrook, Manchester.

Alexander McDougall, Esq., Dawson Street, Manchester.

J. Frederick Davis, Esq., Fountain Street, Ulverston, Lancashire.

R. S. Roper, Esq., Ebbw-Vale, Newport, Monmouthshire.

The following Gentleman was elected an Associate of the Society :—

Dr. Evan Pugh, Rothamstead.

Dr. Frankland exhibited some specimens of Mr. Gore's Explosive Antimony, and illustrated its properties.

Papers were read :—

"On the existence of a new Crystallizable Fluorescent Substance, Paviin, in the bark of the Horse-chestnut tree:" by Professor Stokes, Sec. R. S.

"On a new Maximum and Minimum Thermometer:" by the Rev. J. G. Macvicar, D.D.

Dr. Odling, Secretary to the Chemical Society, described the formation of some Common Salt, crystallised by cooling a hot hydrochloric solution.

Dr. Versmann exhibited some new forms of Chemical Apparatus.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

Researches on a New Class of Alcohols.

By Augustus William Hofmann and Augustus Cahours.

Abstracted from a Paper read before the Royal Society June 18. 1857.

ON submitting glycerin to destructive distillation, either alone or in the presence of bisulphate of potassium or anhydrous phosphoric acid, a very remarkable product is obtained, which has been elaborately studied by Professor Redtenbacher. According to the researches of this distinguished chemist, this substance, to which the name of acrolein has been given, presents all the characters of an aldehyde, and bears, in its reactions, a close resemblance to the vinic aldehyde. Under the influence of oxidizing agents, and especially of oxide of silver, this body changes into an acid which Redtenbacher designates by the name "Acrylic Acid," and which bears the same relation to acrolein that is observed between acetic acid and common aldehyde.

The researches of Messrs. Will and Wertheim upon the volatile oils of garlic and mustard, established a relationship between these compounds and acrolein, which has been rendered still more evident by the recent very interesting investigations of Messrs. Berthelot and De Luca. In studying the action of iodide of phosphorus upon glycerin, these chemists obtained a volatile liquid containing iodine, the composition of which is expressed by the formula C_6H_5I , and to which they applied the name Iodide of Propylene. This substance is evidently allied to the chloride of propylene C_6H_5Cl , and bromide of propylene, C_6H_5Br , discovered previously by Messrs. Cahours, Reynolds, and Hofmann, in studying the action of chlorine and bromine on the gases which are obtained by submitting either amylic alcohol or valeric acid, as well as their higher homologues, to the action of heat.

A glance at the formulæ of the propylene-compounds, and the volatile oils of garlic and mustard, viz.

| | | | |
|-----------------------|---|---|-------------------|
| Chloride of propylene | . | . | C_6H_5Cl , |
| Bromide of propylene | . | . | C_6H_5Br , |
| Iodide of propylene | . | . | C_6H_5I , |
| Garlic oil | . | . | C_6H_5S , |
| Mustard oil | . | . | $C_6H_5C_2NS_2$, |

obviously shows that the same radical Allyl, C_6H_5 , may be assumed to exist in all these compounds.

This relation did not escape Mr. Reynolds, who, in his memoir published about six years ago,* distinctly sets forth the probability of the transformation of the chloride and bromide of propylene into the oils of garlic and mustard by the action respectively of the sulphide and sulphocyanide of potassium. The experimental accomplishment of this idea was however reserved at a later period to Messrs. Berthelot and De Luca, and to M. Zinin. In fact, these chemists demonstrated that the action of iodide of propylene upon the sulphocyanides of potassium or silver, gives rise to an oil which is absolutely identical with that furnished by distilling with water the seeds of the common mustard (*Sinapis nigra*).

The admission of a radical allyl (C_6H_5) analogous to ethyl (C_4H_5), establishes a perfect analogy between the compounds derived from propylene and glycerin, and the several terms of the ethyl-series.

Ethyl-series.

| | | | | | | | | |
|-------------------|---|---|---|---------------|---|---|---|-----------------|
| C_4H_5Cl | . | . | . | Chloride | . | . | . | C_6H_5Cl |
| C_4H_5Br | . | . | . | Bromide | : | . | . | C_6H_5Br |
| C_4H_5I | . | . | . | Iodide | . | . | . | C_6H_5I |
| C_4H_5S | . | . | . | Sulphide | . | . | . | C_6H_5S |
| C_4H_5, C_2NS_2 | . | . | . | Sulphocyanide | . | . | . | $C_6H_5C_2NS_2$ |
| $C_4H_6O_2$ | . | . | . | Alcohol | . | . | . | |
| $C_4H_4O_2$ | . | . | . | Aldehyde | . | . | . | $C_6H_4O_2$ |
| $C_4H_4O_4$ | . | . | . | Acid | . | . | . | $C_6H_4O_4$ |

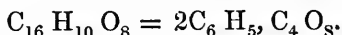
Allyl-series.

There yet remained the key-stone to be inserted into this edifice, in other words, there was to be discovered the alcohol to which not only all the preceding compounds could be referred, but which might serve in producing a long series of substances analogous to the host of compound ethers derived from common alcohol.

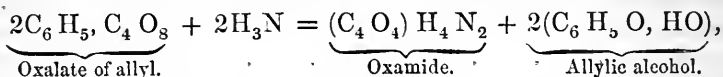
After many attempts, which remained long unsuccessful on account of the facility with which this class of bodies is altered, we at last succeeded in obtaining, not only the alcohol and ether of this series, for which we have adopted the name of the "Allyl-series," but also a very considerable number of compound ethers, and some of their derivatives. In order to arrive at this result, we have submitted a number of silver-salts to the action of iodide of allyl, expecting to obtain by double decomposition iodide of silver and a compound ether, from which it would be possible afterwards to extract the alcohol. The silver-salts are in general powerfully attacked by iodide of allyl, but comparatively few of the products obtained in this reaction are themselves appropriate for the separation of allylic alcohol. The most satisfactory results we have obtained with oxalate of allyl. Iodide of allyl acts very energetically upon oxalate of silver. After several hours' digestion at 100° , which is most conveniently accomplished in the presence

* Quarterly Journal of the Chemical Society, vol. iii. p. 111. 1851.

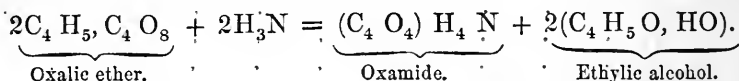
of anhydrous ether, the reaction is completed. The oxalate of allyl furnished by this process can be easily purified; on filtering the ethereal liquor from the iodide of silver and distilling, the ether passes over first, the temperature then rises rapidly, and between 205° and 207° , a colourless transparent liquid distils over, which is the oxalate of allyl. According to our analysis, this ether contains



When once the oxalate of allyl has been procured, nothing is easier than to separate from it the allylic alcohol. It is only necessary to treat this product with an excess of dry ammonia, by which oxamide and the allylic alcohol are obtained, according to the following equation:—



a result in perfect accordance with the reciprocal action of ammonia and oxalic ether:—



The alcohol separated by distillation from the oxamide is not absolutely pure; it may retain water and ammonia; a simple rectification from anhydrous sulphate of copper is sufficient to render it perfectly pure.

Allylic alcohol is a colourless, very mobile liquid, possessing a pungent odour, recalling at the same time that of common alcohol and of mustard oil. It boils at 103°C.^* and is combustible, but burns with a far more luminous flame than ordinary alcohol. Its flavour is spirituous and pungent. Water, alcohol, and wood-spirit dissolve it in all proportions.

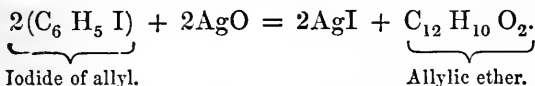
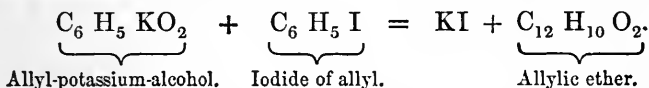
* Here may be mentioned an observation only lately made and not yet further elaborated. At the desire of Professor Kopp, who, in the course of his researches, wished to enter more minutely into the study of the physical properties of allylic alcohol, I have reprepared this body on a larger scale, and with particular care. The liquid obtained by the decomposition of perfectly pure oxalate of allyl having a constant boiling point of 207° began to boil as low as 90° ; the boiling point was most constant at 93° ; at 100° the whole of the liquid had distilled. I would not hesitate to ascribe this discrepancy from the boiling point previously observed to an error of observation, that might have occurred in the first observation, unless the differences of boiling points generally observed between the ethyl and allyl-compounds, suggested rather a higher boiling point than 103° for allylic alcohol. Should this lower boiling point have been occasioned by a metamorphosis of this body? Similar strange, and unexpected changes we have repeatedly observed in allyl-compounds, and especially among the products of decomposition of cyanate of allyl. Further experiments are required to solve this question.

The analysis* of allylic alcohol has led to the formula

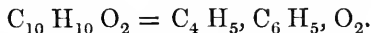


Accordingly, allylic alcohol has the same composition as acetone and propylic aldehyde, from both of which substances it nevertheless essentially differs.

Potassium and sodium attack allylic alcohol energetically, especially if the temperature be slightly raised; hydrogen is copiously evolved, and a gelatinous substance is formed obviously analogous to potassium-alcohol, the composition of which must accordingly be represented by the formula $C_6 H_5 KO_2$. On treating this last product with iodide of allyl, much heat is evolved, iodide of potassium is deposited in abundance, and at the same time there is formed a colourless volatile liquid, very mobile, lighter than water and entirely insoluble in that menstruum, which corresponds both in composition and reactions to ordinary ether. This compound, which we will designate by the term allylic ether, and which boils at $82^\circ C.$, also results from the reaction of iodide of allyl on the oxides of silver and mercury. The following equations represent these reactions:—



On treating ethylic potassium-alcohol with iodide of allyl, or allylic potassium-alcohol with iodide of ethyl, iodide of potassium is deposited, a colourless, aromatic, very volatile liquid being formed, which boils at about $64^\circ C.$, and is a mixed ether containing both the radicals ethyl and allyl, and represented by the formula



Methyl-, amyl- and phenyl-potassium-alcohols, when brought in contact with iodide of allyl, furnish analogous results.

By distilling allylic alcohol with the chloride, bromide, or iodide of phosphorus, the hydrochloric, hydrobromic and hydriodic ethers of this series are obtained with the utmost facility. Iodide of allyl obtained by this process, possesses all the properties of the iodide of propylene which is produced by the action of iodide of phosphorus on glycerin; and in a similar manner, the chloride and bromide of allyl, and the chloride and bromide of propylene, are identical in every respect.

* The analytical details are given in the Philosophical Transactions for 1857.

Allylic alcohol dissolves without coloration in concentrated sulphuric acid, and gives rise to a conjugate acid which forms soluble and crystalline salts with baryta, strontia, and oxide of lead. Anhydrous phosphoric acid powerfully attacks allylic alcohol at a moderate temperature, a colourless gas being disengaged which burns with a very luminous flame. Its analysis has not been made, but to all appearance it is a hydrocarbon represented by the formula C_6H_4 .

Allylic alcohol is readily acted upon by oxidizing agents. A mixture of bichromate of potassium and sulphuric acid attacks this body with extreme violence. The products of the reaction are acrolein and allylic acid. The same transformation is effected by platinum-black, though more slowly. Lastly, this alcohol, when treated with potassa and bisulphide of carbon, gives rise to a compound which crystallizes in beautiful yellow needles, resembling xanthate of potassium, and to which analysis will probably assign an analogous formula.

Sulphide of Allyl (Essence of Garlic).—When iodide of allyl is allowed to fall drop by drop into a concentrated alcoholic solution of protosulphide of potassium, a very energetic action ensues, the liquid becomes very hot, and an abundant crystalline deposit takes place of iodide of potassium. It is important that the iodide of allyl should only be added gradually, to avoid spirting, by which a part of the product would be lost. As soon as the action ceases, the liquid is mixed with a slight excess of sulphide of potassium; addition of water now separates a light yellowish limpid oil, possessing a strong smell of garlic. When rectified, this liquid becomes colourless; it boils at $140^\circ C.$, and gives with nitrate of silver a crystalline precipitate soluble in a boiling mixture of alcohol and water, and separating from this solvent in the form of beautiful white needles, absolutely identical with those which the natural essence of garlic produces. Sulphide of allyl also comports itself with corrosive sublimate and bichloride of platinum, exactly like the natural garlic oil.

Formula: $C_{12}H_{10}S_2 = 2C_6H_5S.$

Allylic Mercaptan.—When in the process for the preparation of the preceding compound, the protosulphide of potassium is replaced by the hydrosulphate of sulphide of potassium, a volatile product is obtained, having a similar but more ethereal odour. This substance acts with energy upon oxide of mercury, with which it forms a compound dissolving in boiling alcohol and separating from it on cooling in the form of pearly scales of remarkable brilliancy, which present the greatest resemblance to mercaptide of mercury. The liquid obtained in the above-mentioned reaction boils at 90° , and possesses a composition and an aggregate of pro-

perties which closely resemble those of the mercaptan of the ethyl-series, being in fact the allylic mercaptan.

Formula : $C_6 H_6 S_2$.

This compound is powerfully attacked by nitric acid, with disengagement of binoxide of nitrogen; the liquid assumes a red colour in the same manner as ethylic mercaptan, the product of the reaction being a peculiar acid, analogous to ethylosulphurous acid, which forms with baryta a salt crystallizing in brilliant white scales.

Sulphallylic Acid.—When allylic alcohol is added in small quantities at a time to about its own volume of monohydrated sulphuric acid, the mixture becomes heated without being sensibly coloured. If the acid liquor be diluted with about seven to eight times its volume of water, and then neutralized with carbonate of barium in fine powder, there is obtained on evaporation a substance which crystallizes in brilliant white laminæ. This salt, which is formed under the very same conditions as sulphovinate of barium, is represented by the formula



Oxalate of Allyl and Allyloxamethan.—We have previously stated under what circumstances oxalate of allyl is formed; we will not therefore recur again to its mode of preparation. Purified by a simple rectification, this compound presents itself as a colourless limpid liquid of a specific gravity of 1.05 at 15°.5, and boiling constantly between 206° and 207° C. (Bar. 0^m.754), possessing an aromatic odour recalling that of oxalic ether, with a faint admixture of the smell of mustard oil. A similar remark in fact applies to all the allyl-compounds; they smell like the corresponding ethyl-compounds, only somewhat more pungent. When mixed with water, oxalate of allyl undergoes gradual decomposition, but it is much more rapidly decomposed when boiled with a solution of caustic potassa. Solution of ammonia attacks it rapidly, and transforms it into oxamide and allylic alcohol. An alcoholic solution of ammonia added with caution, so as to avoid the formation of oxamide, produces a substance analogous to oxamethan, which, for this reason, we shall designate by the name allyloxamethan. This substance separates in magnificent crystals, when its alcoholic solution is allowed to evaporate spontaneously.

Potassium and sodium energetically attack the oxalate of allyl, especially with the aid of heat; an evolution of carbonic oxide ensues, whilst there passes over on distillation a limpid colourless oil of an aromatic odour lighter than water; this is in fact the carbonate of allyl.

Formula of oxalate of allyl : $C_{16} H_{10} O_8 = 2C_6 H_5, C_4 O_8$.

Formula of allyloxamethan : $C_{10} H_7 NO_6 = C_6 H_5, C_4 NH_2 O_6$.

Acetate of Allyl.—Iodide of allyl, when brought in contact with acetate of silver, becomes strongly heated, producing iodide of the metal and a liquid of an aromatic odour which closely resembles that of acetic ether. The crude product obtained in this way is not pure; it always retains a certain quantity of the iodide of allyl, from which it is purified by one or two rectifications over a fresh quantity of acetate of silver.

Thus prepared, acetate of allyl is a colourless liquid lighter than water, possessing a pungent aromatic smell, and boiling between 98° and $100^\circ C$. Potassa decomposes it at the boiling temperature, giving rise to the formation of acetate of potassium and reproducing allylic alcohol.

Formula : $C_{10} H_8 O_4 = C_6 H_5, C_4 H_3 O_4$.

Butyrate of Allyl.—Iodide of allyl becomes strongly heated when brought into contact with butyrate of silver; when the mixture is distilled, an amber-coloured liquid is collected, which becomes colourless by rectification. This liquid is oily, very limpid, lighter than water, boils at about $140^\circ C$., and has an odour suggestive of butyric ether. Concentrated solution of potassa decomposes this ether rapidly when assisted by heat, producing allylic alcohol and an alkaline butyrate.

Formula : $C_{14} H_{12} O_4 = C_6 H_5, C_8 H_7 O_4$.

Valerate of Allyl.—Valerate of silver comports itself with iodide of allyl exactly like the acetate and butyrate: powerful reaction, attended by separation of iodide of silver, and generation of an ethereal liquid; which may be obtained pure by repeated rectification over fresh quantities of valerate of silver, washing with slightly alkaline water, and digestion over chloride of calcium. Thus prepared, valerate of allyl is a colourless liquid which boils at 162° , and the aromatic odour of which recalls that of valerate of ethyl. It is lighter than water, insoluble in this menstruum, but readily dissolved by alcohol and ether. The vapour burns with a luminous flame.

Formula : $C_{16} H_{14} O_4 = C_6 H_5, C_{10} H_9 O_4$.

Benzoate of Allyl may be obtained either by the action of chloride of benzoyl on allylic alcohol, or by the action of iodide of allyl on benzoate of silver. It is a nearly colourless liquid with a tinge of amber, heavier than water, in which fluid it is insoluble; it possesses an aromatic odour similar to that of

benzoic ether, and boils at 228°C . Alcohol, wood-spirit, and ether dissolve it freely. A boiling aqueous solution of potassa decomposes it, reproducing allylic alcohol and benzoic acid, which unites with the alkali.

Formula: $\text{C}_{20} \text{H}_{10} \text{O}_4 = \text{C}_6 \text{H}_5, \text{C}_{14} \text{H}_5 \text{O}_4$.

Cyanate of Allyl.—Cyanate of silver is rapidly attacked, even in the cold, by iodide of allyl, the heat generated by the reaction being sufficient to carry over nearly the whole of the product. By this means, a colourless, very limpid liquid is obtained, boiling at 82° , and possessing an extremely pungent odour, which, like that of cyanic ether, produces lacrymation in a high degree. When mixed with ammonia, this substance rapidly disappears, a gentle evolution of heat being perceptible, and the solution furnishes on evaporation a magnificent crystallized body which is the allylic urea. Ethylamine behaves in a similar manner with cyanate of allyl, and on evaporation beautiful prisms of ethyl-allyl urea are obtained.

Formula of cyanate of allyl: $\text{C}_8 \text{H}_5 \text{NO}_2 = \text{C}_6 \text{H}_5, \text{C}_2 \text{NO}_2$.

We have controlled the preceding formula by a determination of the density of the vapour of cyanate of allyl.

The experimental vapour density was found to be 3.045.

The weight represented by the formula $\text{C}_8 \text{H}_5 \text{NO}_2$, divided by the experimental density, furnishes the quotient $\frac{83}{3.045} = 27.25$. For a condensation to four volumes of vapour, the more accurate number 28.92 should have been found. Thus it is obvious that the condensation to four volumes observed for most organic substances, obtains also with cyanate of allyl. The theoretical density of the vapour of cyanate of allyl is $\frac{83}{28.92} = 2.87$.

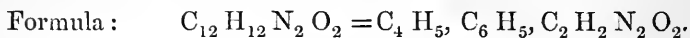
Allyl-Urea.—The formation of this substance has already been mentioned. On submitting a solution of cyanate of allyl in ammonia to evaporation, a beautifully crystallized colourless substance is obtained, which is soluble in water and alcohol.

Formula: $\text{C}_8 \text{H}_8 \text{N}_2 \text{O}_2 = \text{C}_6 \text{H}_5, \text{C}_2 \text{H}_3 \text{N}_2 \text{O}_2$.

It differs from thiosinamine only in having the sulphur of this substance replaced by an equivalent proportion of oxygen. This compound which is prepared under conditions which determine the production of ureas, presents all the properties of this class of compounds.

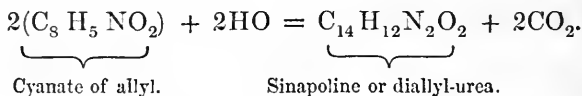
Ethyl-allyl-urea.—On replacing in the transformation of the cyanate of allyl, ammonia by solution of ethylamine, a series of perfectly analogous phenomena is observed. On cooling, the fluid solidifies into a crystalline mass, which dissolves in alcohol, and separates from this solution on evaporation,

in the form of beautiful prisms similar to those of allyl-urea. This substance is ethyl-allyl-urea.



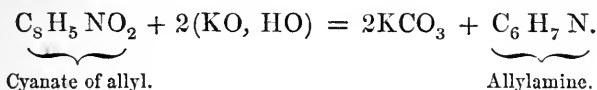
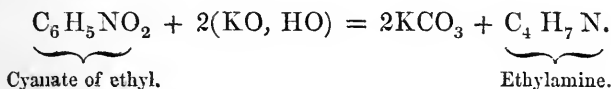
The action of methylamine, of amylamine, and of aniline upon cyanate of allyl, has furnished us analogous results. We have not submitted these products to analysis; but their resemblance to the preceding compounds, and especially their mode of formation, leave no doubt respecting their composition. These products, as is obvious, belong to that numerous class of compound ureas which have been studied with such remarkable results by M. Wurtz.

Diallyl-urea (Sinapoline).—When cyanate of allyl is heated with water, it assumes a buttery consistence and ultimately solidifies entirely. The product obtained under these circumstances possesses all the properties of sinapoline, which, as is known, is formed by the action of hydrated protoxide of lead upon mustard oil, and is, in fact, diallyl-urea. The properties of this substance presenting complete identity with those of sinapoline, and its mode of formation being perfectly similar to that of dimethyl- and diethyl-urea, we have not thought it necessary to submit it to analysis. This body is likewise formed when cyanate of allyl is boiled with an aqueous solution of potassa, with a view of transforming it, after the manner of ordinary cyanic ether, into an alkaline carbonate and an ammonia-base. In this case, it is necessary to arrest the action at a certain point; for if the ebullition be continued, the sinapoline is destroyed in its turn, producing carbonate of potassium and ammonia-bases. The formation of sinapoline, by the reciprocal action of cyanate of allyl and water, is represented by the following equation:—



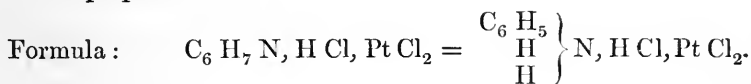
Allyl-ammonias.—When cyanate of allyl is boiled with a concentrated solution of caustic potassa until the oily layer entirely disappears, a complete decomposition ensues, and the residue contains only a mixture of carbonate of potassium with an excess of the alkaline hydrate; the volatile products condensed in hydrochloric acid furnish a saline mass which may be obtained crystallized by evaporation. This substance is always a mixture, the constituents of which vary both in nature and proportions. The action of potassa on it always produces a base which is readily soluble in water, but also basic oils, insoluble in water, the boiling point of which rises as high as 180° C. Simple distillation of the liberated bases appears to give rise to decomposition, and thus

to induce further complication. We have not succeeded in ascertaining with perfect precision the nature of this mixture; but we have found that it invariably contains a considerable quantity of a base which bears the same relation to allylic alcohol that is observed between ethylamine and ordinary alcohol. The formation of this substance, which we propose to designate *allylamine*, is perfectly analogous to the production of ethylamine by means of cyanate of ethyl:—



But, as we have already said, the decomposition of the cyanate of allyl is far from presenting the same definite character as that of the corresponding compound of the ethyl-series. Since it was impossible to separate the mixture of bases by a fractional distillation, we have determined the composition of allylamine by the analysis of the platinum-salts.

Allylamine.—On adding solution of bichloride of platinum to the hydrochloric solution of the bases resulting from the action of potassa upon cyanate of allyl, there is produced almost invariably a pale yellow precipitate; and the solution filtered off from this precipitate, deposits on evaporation a magnificent salt, crystallizing in brilliant orange-coloured needles. The pale precipitate* varies in quantity and composition; but the second salt has a perfectly definite and constant composition, it is soluble in water and may be re-crystallized from it. The analyses of samples of different preparations led to the



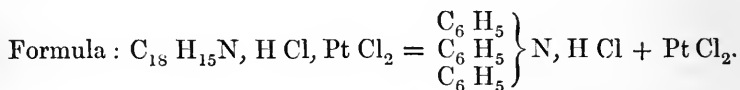
The same body is likewise formed by the action of ammonia upon the iodide of allyl. On distilling the product of this reaction with potassa, ammonia is disengaged; but towards the end of the operation, an alkaline liquid distils over, which no longer contains ammonia, and upon which there floats a small quantity of a basic oil. On saturating the aqueous solution, together with the

* From numerous analyses, this precipitate appears to be a mixture in variable proportions of the platinum-salts of ammonia and methylamine.

oil, with hydrochloric acid, and adding bichloride of platinum, the platinum-salt of allylamine separates, either directly if the solution be concentrated, or gradually in magnificent gold-coloured needles, if the liquid be gently evaporated.

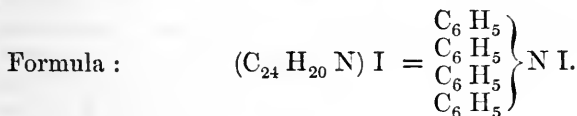
Diallylamine.—Impure allylamine, obtained either by the action of potassa on the cyanate, or of ammonia on the iodide of allyl, when digested with a second quantity of iodide of allyl, is rapidly changed into a mass of hydriodates of new compounds. This crystalline mass evidently contains a considerable quantity of the hydriodate of diallylamine; but to succeed in separating it from this very complicated mixture, would have required a considerable quantity of substance. We have therefore been satisfied to determine by a few experiments the existence of triallylamine and the oxide of tetrallylammmonium.

Triallylamine.—The oxide of tetrallylammmonium, to which we shall presently allude, submitted to the action of heat, is decomposed with liberation of a basic oil. The experiment was not made on a sufficient scale to admit of studying the complementary products. The perfect analogy of the oxide of tetrallylammmonium with the corresponding ethyl-compound, leaves no doubt respecting the nature of the basic substance which results from its decomposition by the action of heat. This body must obviously be triallylamine, and experiment has confirmed this anticipation. The base saturated with hydrochloric acid and mixed with bichloride of platinum, deposits a yellow platinum-salt, the analysis of which led to the

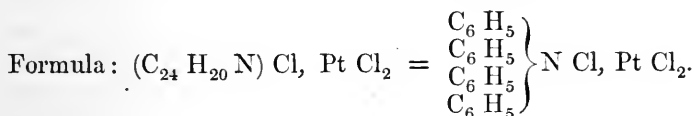


Hydrated Oxide of Tetrallylammmonium.—The chief product of the action of ammonia upon iodide of allyl is a magnificent crystalline compound, which is deposited from the solution resulting from the reaction. We have treated iodide of allyl with ammonia in sealed tubes, but this is not necessary, for iodide of allyl is rapidly attacked even by an aqueous solution of ammonia at the common temperature. By a few days' contact, a large quantity of the iodide dissolves, and the solution sometimes becomes a solid mass. If no deposition of crystals take place from the solution, it is only necessary to add a concentrated solution of potassa; this causes the separation of an oily layer which speedily solidifies. The crystals thus formed are the iodide of tetrallylammmonium,

which, like the corresponding compound of the ethyl- and methyl-series, is but slightly soluble in solution of potassa. It is obtained pure by exposing it to the air until the potassa is converted into carbonate, and then recrystallizing it from absolute alcohol.

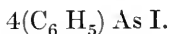


The iodide, treated with oxide of silver, is immediately transformed into the oxide. This forms an alkaline solution, which possesses all the properties of the hydrated oxide of tetraethylammonium. When it is mixed with hydrochloric acid and bichloride of platinum, a pale yellow precipitate is obtained, of the



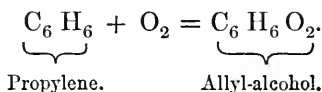
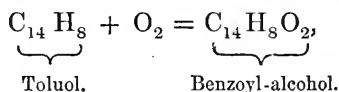
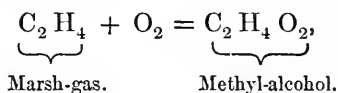
The examination of the allylamines leaves yet much to be accomplished; we have not succeeded in separating these bodies from one another with sufficient accuracy to give a precise account of the physical properties of the different terms of this series; nevertheless, our experiments prove the existence in the allyl-series of four compounds analogous to the four bases of the ethyl-series.

Iodide of Tetraallylarsonium.—Iodide of allyl attacks arsenide of potassium, but far less energetically than iodide of ethyl; several liquid compounds, of a very fetid odour, are produced, the boiling-points of which, however, extend over so considerable a range of the scale, that we had to abandon the idea of studying them. But, at the same time, a solid crystalline body is formed, which is obviously iodide of tetraallylammonium, in which the nitrogen is replaced by arsenic:—

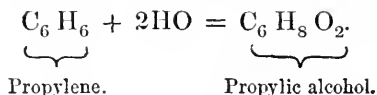
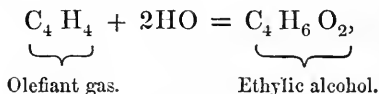


On taking a retrospective glance at the preceding results, it is obvious that propylene, a homologue of olefiant gas, is susceptible of furnishing a mono-acid alcohol and its derivatives, which bears to

it the same relation that is observed between methyl-alcohol and marsh-gas, or between benzoic alcohol and toluol, the analogue of marsh-gas among the derivatives of the aromatic acids. The hydrocarbons homologous with, and analogous to marsh-gas, the homologues of olefiant gas, and, indeed, probably a very considerable number of other similarly constituted hydrocarbons, may be regarded as starting-points for the preparation of mono-acid alcohols and of all their derivatives. All these alcohols are formed by the fixation of two equivalents of oxygen, which oxidation, however, cannot yet be effected directly, but is accomplished by a series of substitution-processes.



Olefiant gas and its homologues are capable of furnishing mono-acid alcohols by another reaction, which has not yet been applied to the series of bodies homologous with marsh-gas. In fact, we have learnt by the beautiful researches of M. Berthelot, that olefiant gas and its homologues are capable of being transformed into alcohols by the absorption of two equivalents of water; olefiant gas furnishes by this reaction ordinary alcohol, and propylene, propylic alcohol; thus—



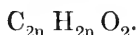
Olefiant gas, then, and all of its homologues, are capable of furnishing *two* mono-acid alcohols, exhibiting slightly different features, but presenting in all their principal characters the most obvious analogies. The alcohols formed by fixation of water, such as ethylic alcohol, have been long well known; in fact, the detailed study which has been made during the last quarter of a

century of most of their derivatives, has exercised the most beneficial influence upon the development of organic chemistry.

The same remark does not apply to the alcohols produced from these same hydrocarbons by fixation of oxygen. The history of allylic alcohol, which we have endeavoured to trace in the preceding pages, and to which of late important contributions have been furnished, moreover, by MM. Berthelot and De Luca and by M. Zinin, begins also to throw light upon this second group of alcohols. For this reason, the discovery of allylic alcohol appears to claim the attention of chemists, even had it not assisted in fixing, in the system of organic compounds, the exact position of several very interesting natural products, viz. the sulphuretted oils furnished by the bulbs of the garlic (*Allium sativum*) and the seeds of the black mustard (*Sinapis nigra*), which it had not been possible up to the present time to group round a similar centre.

It is highly probable that by submitting the various hydrocarbons polymeric with propylene to appropriate reactions, other alcohols may be obtained homologous with allyl-alcohol. This much is certain, that by distilling a mixture of cyanate of silver and bromide of amylene $C_{10}H_9Br$, a volatile liquid is obtained, which possesses an extremely irritating odour, provoking lachrymation like the cyanic ethers. This forms by contact with ammonia a crystallizable urea, which, when decomposed by potassa, yields, like cyanate of allyl, bases, among which the compound $C_{10}H_{11}N$ may be traced.

Allylic alcohol, the history of which we have endeavoured to sketch, forms the third term of a series of alcohols, which may be represented by the general formula,



In fact, a group of homologous acids is known, which, according to their composition, bear the same relation to acetic acid and its homologues, that is observed between our new group of alcohols, and the alcohol series commencing with methylic and ethylic alcohols. In addition to acrylic acid, angelic and oleic acids are the best known terms of this group of acids. It is possible that cyanide of allyl which is formed by the double decomposition of iodide of allyl and cyanide of silver, but which we have not yet been able to obtain in a state of sufficient purity to admit of analysis, may be transformed by boiling with a solution of caustic potassa into an acid homologous with acrylic acid, in the same way as cyanide of propyl is resolved under similar circumstances into butyric acid.

The following Table exhibits in a more conspicuous manner the two groups of alcohols and acids.

| Alcohols. | | Acids. | |
|-----------------------------------|---------------------------|------------------------------------|------------------------------|
| $C_2 H_4 O_2$ Methylic. | $C_2 H_2 O_2$ | $C_2 H_2 O_4$ Formic. | |
| $C_4 H_6 O_2$ Ethylic | $C_4 H_4 O_2$ | $C_4 H_4 O_4$ Acetic. | $C_4 H_2 O_4$ |
| $C_6 H_8 O_2$ Propylic. | $C_6 H_6 O_2$ Allylic. | $C_6 H_6 O_4$ Propionic. | $C_6 H_4 O_4$ Acrylic. |
| $C_8 H_{10} O_2$ Butylic. | $C_8 H_8 O_2$ | $C_8 H_8 O_4$ Butyric. | $C_8 H_6 O_4$ |
| $C_{10} H_{12} O_2$ Amylic. | $C_{10} H_{10} O_2$ | $C_{10} H_{10} O_4$ Valeric. | $C_{10} H_8 O_4$ Angelic. |
| $C_{12} H_{14} O_2$ Caproylic. | $C_{12} H_{12} O_2$ | $C_{12} H_{12} O_4$ Caproic. | $C_{12} H_{10} O_4$ |
| $C_{14} H_{16} O_2$ | $C_{14} H_{14} O_2$ | $C_{14} H_{14} O_4$ Enanthylic. | $C_{14} H_{12} O_4$ |
| $C_{16} H_{18} O_2$ Caprylic. | $C_{16} H_{16} O_2$ | $C_{16} H_{16} O_4$ Caprylic. | $C_{16} H_{14} O_4$ |
| — | — | — | — |
| — | — | — | — |
| — | — | — | — |
| — | — | — | — |
| $C_{36} H_{33} O_2$ | $C_{36} H_{36} O_2$ | $C_{36} H_{36} O_4$ Stearic. | $C_{36} H_{34} O_4$ Oleic |

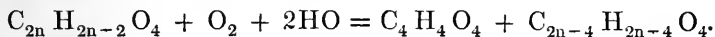
A glance at this Table shows how very few representatives of the series of alcohols $C_{2n} H_{2n} O_2$, and acids $C_{2n} H_{2n-2} O_4$, have as yet been observed. The progress of science will not fail to fill up the numerous gaps.

Even now some bodies are known which are most intimately connected with the preceding series. Indeed, cinnamic alcohol and cinnamic acid belong to a group of substances bearing to the aromatic alcohols and acids the same relation which obtains between the allyl-compounds and their homologues, and the alcohols and acids of the fatty bodies.

| Alcohols. | | Acids. | |
|---------------------------------|----------------------------------|---------------------------------|-------------------------------|
| $C_{14} H_8 O_2$ Benzoic. | $C_{14} H_6 O_2$ | $C_{14} H_6 O_4$ Benzoic. | $C_{14} H_4 O_4$ |
| $C_{16} H_{10} O_2$ | $C_{16} H_8 O_2$ | $C_{16} H_8 O_4$ Toluic. | $C_{16} H_6 O_4$ |
| $C_{18} H_{12} O_2$ | $C_{18} H_{10} O_2$ Cinnamic. | $C_{18} H_{10} O_4$ | $C_{18} H_8 O_4$ Cinnamic. |
| $C_{20} H_{14} O_2$ Cuminic. | $C_{20} H_{12} O_2$ | $C_{20} H_{12} O_4$ Cuminic. | $C_{20} H_{10} O_4$ |

From this table again it is manifest how many substances remain still to be discovered in this direction. Cinnamic acid contains two equivalents of hydrogen less than the acid $C_{18} H_{10} O_4$, which will be discovered between toluic and cuminic acids. It stands to this acid in the same relation which is observed between acrylic and propionic acids.

The acids belonging to the acrylic group all possess the property of being transformed, by fixation of two atoms of oxygen and two of water, into acetic acid and a second homologous acid, as is shown by the following equation:—



It is thus that acrylic, angelic, and oleic acids are resolved, under the influence of hydrate of potassa at a temperature of $200^\circ C.$, into acetic acid, and on the other hand into formic, propionic, and ethalic acids.

Cinnamic acid suffers under the influence of potassa a perfectly analogous transformation. This acid fixes two equivalents of water, and yields acetic and benzoic acids.

In carrying out the preceding inquiry, we have been very ably assisted by Mr. Arthur H. Church, to whom our best thanks are due.

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TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1857.

A.

Acetamide.—On some combinations and reactions of acetamide: by *A. Strecker*. Ann. Ch. Pharm. ciii. 321; J. Pharm. [3] xxx. 398.

Acetyl.—On aldehyde and chloride of acetyl: by *A. Wurtz*. Ann. Ch. Phys. [3] xlv. 58; Ann. Ch. Pharm. cii. 93.

— On iodide of acetyl: by *F. Guthrie*. Phil. Mag. [4] xiii. 183; Ann. Ch. Pharm. ciii. 335.

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— On the rational constitution of fulminic acid, and on a new series of bodies derived from acetic acid: by *L. Schischkoff*. Compt. rend. xlv. 14; Chem. Gaz. 1857, 86; Ann. Ch. Phys. [3] xlix. 310; Ann. Ch. Pharm. ci. 213.

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- Acid, Benzotartaric.—On benzotartaric acid: by *V. Dessaignes*. J. Pharm. [3] xxxii. 47.
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- On the gaseous emanations accompanying boracic acid in the *Suffioni* and *Lagoni* of Tuscany: by *C. Deville* and *F. Leblanc*. Compt. rend. xlv. 750, 787.
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- On the quantitative determination of boracic acid: by *A. Stromeyer*. Ann. Ch. Pharm. c. 80; Chem. Gaz. 1857, 50.
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- Acid, Choleic.—See *Acid Hippuric*.
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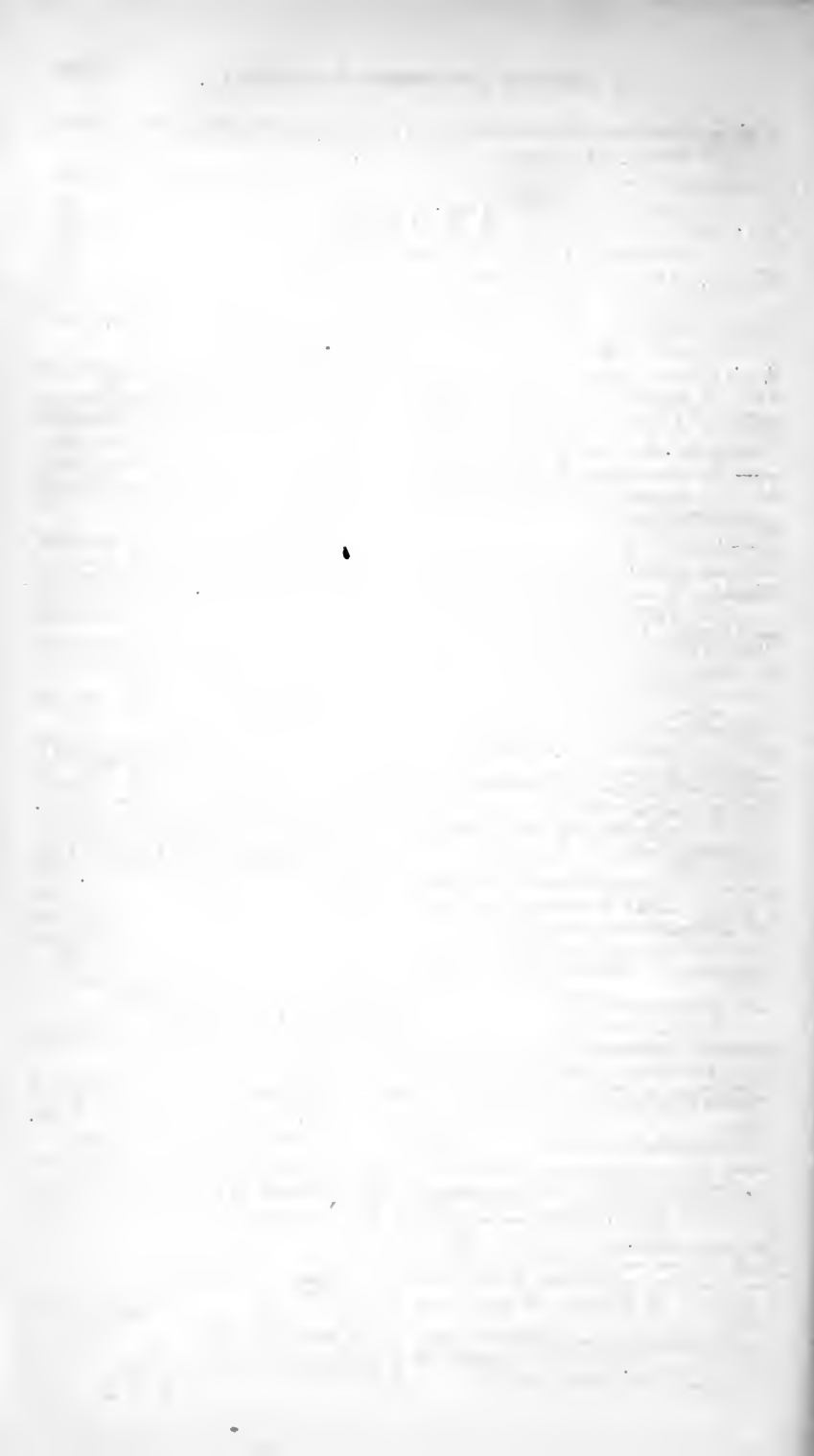
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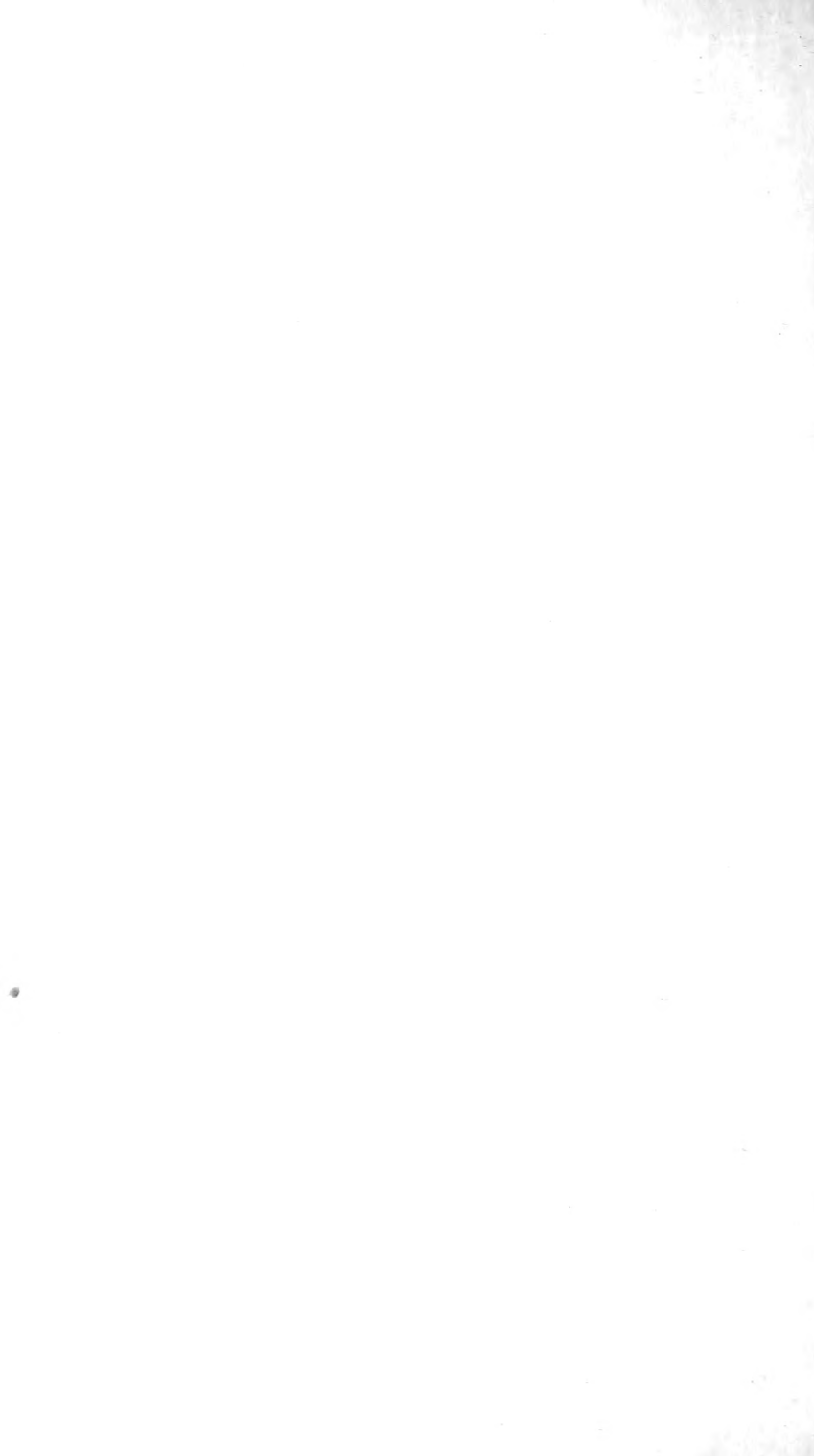
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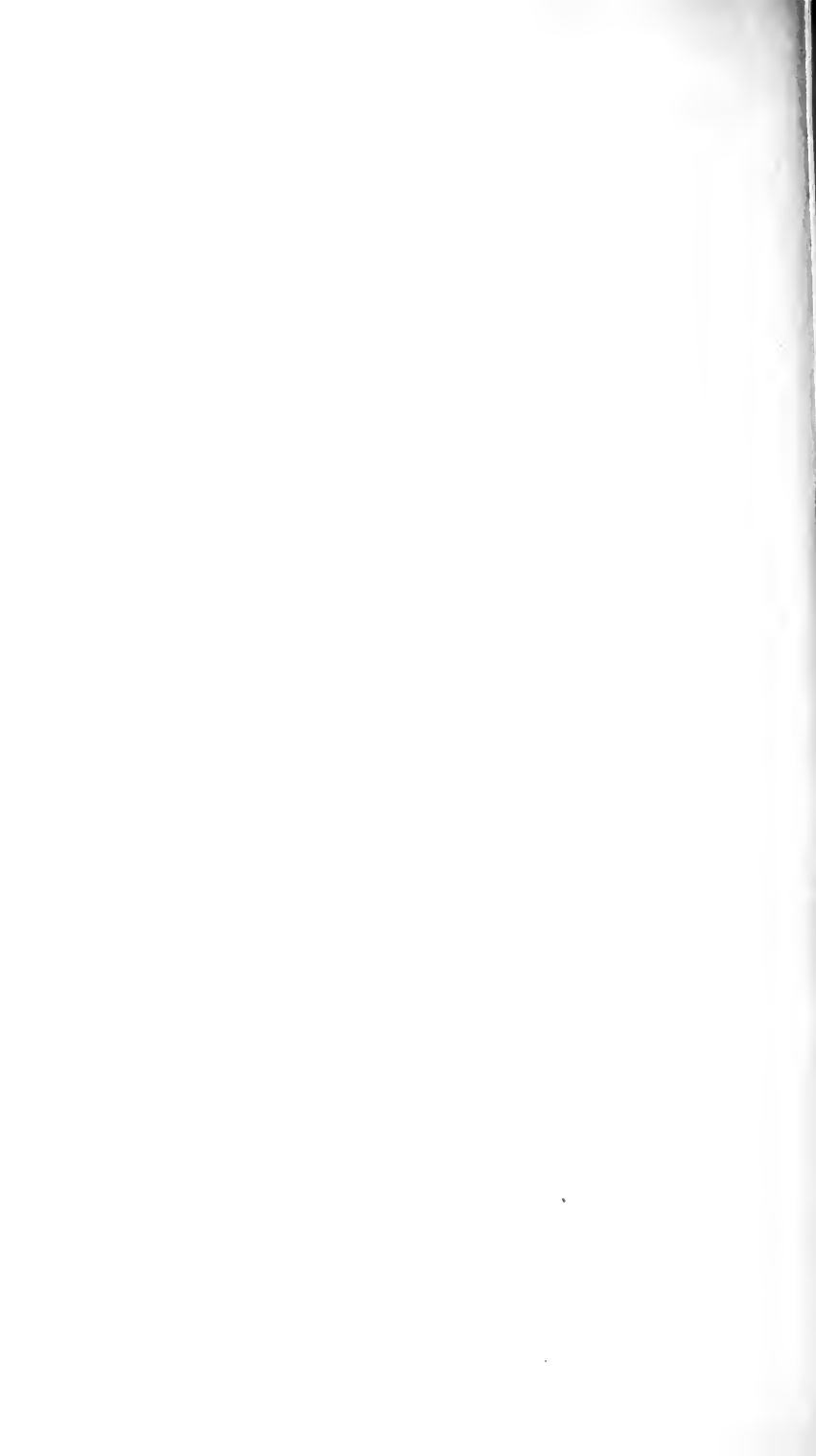
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